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# Canadian Journal of Research

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VOL. 17, SEC. A.

DECEMBER, 1939

NUMBER 12

## THE VISCOSITY OF LIQUID HYDROGEN<sup>1</sup>

By H. E. JOHNS<sup>2</sup>

### Abstract

The viscosity of liquid hydrogen has been measured by observing its flow through a variety of capillary tubes. The resulting viscosities are about 10% higher than those obtained by Keesom and Macwood using an oscillating disc.

### Introduction

The viscosity of liquid helium has recently been measured at Toronto (1) by observing its flow through fine glass capillaries. The values were about 50% higher than those obtained by Keesom and Macwood, using an oscillating disc (2). The author therefore decided to measure the viscosity of liquid hydrogen by the flow method in order to compare the results for this liquid with those of Keesom and Macwood (3). For liquid hydrogen the values obtained by the flow method are approximately 10% higher than those obtained by the oscillating disc method.

### Apparatus

The apparatus employed was essentially the same as that used in the determination of the viscosity of helium (1). Several capillaries were attached to tubular reservoirs, and were mounted on a frame parallel to a scale, as shown in Fig. 1. The whole was arranged so that it could be raised or lowered in a closed vessel of liquid hydrogen to allow the liquid to flow through the capillaries in or out of the reservoirs. The vessel containing the liquid hydrogen used for the experiment was completely surrounded by a bath of liquid hydrogen in the cryostat, and during the experiment the inner vessel was closed off so that no evaporation could take place. The temperature was controlled by pumping on the liquid hydrogen in the outer vessel.

The surface tension of the liquid hydrogen caused the liquid in the reservoirs to come to an equilibrium position (*A*) approximately 1 cm. above the surrounding level (*B*). The pressure head was measured from the equilibrium position rather than from the level of the surrounding liquid. For the finer capillaries the flow took place very slowly so that the equilibrium position was not attained until the elapse of 20 to 30 min. In order to carry out the

<sup>1</sup> Manuscript received September 7, 1939.

Contribution from the McLennan Laboratory, Department of Physics, University of Toronto, Toronto, Canada.

<sup>2</sup> Holder of a Studentship under the National Research Council of Canada.

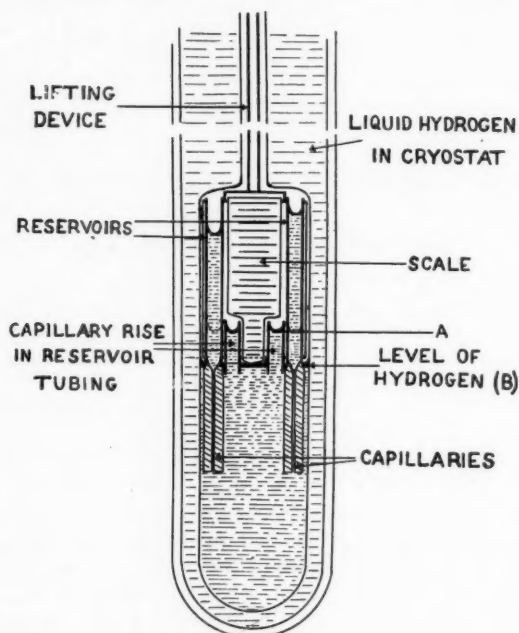


FIG. 1. Diagram of apparatus.

experiment more quickly, in this case, a piece of reservoir tubing open at both ends was placed beside the other reservoirs, so that the capillary rise could be measured directly. The pressure heads were then measured from the level in the open tube (A). To insure complete "wetting" of the reservoirs by the hydrogen, readings were always taken with the liquid flowing out of the reservoirs to the bath, that is, in the position shown in Fig. 1. In the earlier work on liquid helium, the capillary rise was found to be negligible, and no correction was necessary.

The measurements with tubes I *a*, *b*, *c*, were made photographically as described in the previous publication (1) and the pressure head was measured from the equilibrium position finally attained. For tubes II *a* and III *a*, *b*, *c*, the pressure head was measured from the surface in the open reservoir by means of a cathetometer, the time being recorded on a chronograph; the measurements could be made in this way much more accurately, and down to smaller pressure heads. Therefore the results for tubes II and III have been given weight 1 in comparison with weight  $\frac{1}{2}$  for tubes I.

The pressure heads were usually measured from about 5 cm. down to 0.1 cm. When the pressure head was plotted against the time on semilogarithmic paper it was frequently found that the points lay on a straight line over a range from 5 cm. to about 0.5 cm. and then curved slightly up or down for the lower pressure heads. It seemed probable that this was due to an error

in the correction for capillarity. This is confirmed by the fact that the graphs were easily rectified by adding to, or subtracting from, the pressure heads small amounts (usually less than 0.01 cm.) For some of the capillaries the pressure head was corrected for the kinetic energy of efflux but in no case was this greater than  $\frac{1}{2}$  of 1%. When these corrections were made the slopes of the graphs could be determined to better than 1%.

### Results

The viscosity was determined by the use of 7 capillary tubes whose dimensions are given in Table I. The probable errors of the average length and

TABLE I  
DIMENSIONS OF CAPILLARY TUBES

Tube	Length of capillary, cm.	Diameter of capillary, cm.	Diameter of reservoir, cm.
Ia	5.93	0.01676	0.1428
Ib	4.36	0.01205	0.1596
Ic	9.50	0.02340	0.1838
IIa	5.86	0.01590	0.1415
IIIa	3.83	0.01588	0.1415
IIIb	4.38	0.01679	0.1412
IIIc	1.627	0.01196	0.1405

diameter of the capillaries, and of the diameter of the reservoirs were all about 0.2%, so that the results for any one tube had a probable error due to this cause of about 0.9%. The slopes of the graphs could be determined with a

TABLE II  
TEMPERATURE, DENSITY, AND CALCULATED VISCOSITY

Tube	Temperature, °K.	Density, gm./cm. <sup>3</sup>	Viscosity, 10 <sup>-4</sup> c.g.s. units	Tube	Temperature, °K.	Density, gm./cm. <sup>3</sup>	Viscosity, 10 <sup>-4</sup> c.g.s. units
IIIa	20.71	0.07049	136.2	IIIa	18.77	0.07260	160.0
Ia	20.64	0.07056	134.7	IIIa	18.43	0.07295	166.5
Ib	20.64	0.07056	136.0	IIa	18.41	0.07298	165.1
Ic	20.64	0.07056	139.0	IIIc	18.38	0.07295	165.0
IIIb	20.63	0.07058	134.8	IIIb	18.36	0.07303	163.7
IIIa	20.62	0.07059	137.0	IIa	17.96	0.07342	170.2
IIIc	20.29	0.07099	140.5	IIIa	17.80	0.07358	177.2
IIIa	20.28	0.07098	138.7	Ia	17.64	0.07374	172.0
IIIb	20.28	0.07098	140.0	Ib	17.64	0.07374	174.2
Ia	20.10	0.07118	141.1	Ic	17.64	0.07374	176.0
Ib	20.10	0.07118	141.1	IIIa	17.32	0.07405	185.0
Ia	19.61	0.07171	145.5	IIIa	16.88	0.07448	191.4
Ib	19.61	0.07171	146.5	IIIa	16.22	0.07510	204.6
Ic	19.61	0.07171	144.8	Ia	16.16	0.07516	201.0
IIIa	19.61	0.07171	147.4	Ib	16.16	0.07516	204.6
IIIb	19.21	0.07213	151.9	IIIa	15.68	0.07560	217.6
IIIc	19.17	0.07218	151.3	IIIa	15.09	0.07613	229.3
IIIa	19.15	0.07220	152.7	IIIa	14.60	0.07656	238.7
Ia	18.98	0.07238	153.2	Ia	14.60	0.07656	236.8
Ib	18.98	0.07238	150.0	Ib	14.58	0.07658	242.5
Ic	18.98	0.07238	154.2	IIIa	14.29	0.07683	246.6

probable error of about 0.6%, and thus the individual viscosity measurements might be expected to have a probable error of about 1.1%.

Table II contains the temperature, density, and calculated viscosity values for a large number of measurements. These results are also shown in Fig. 2, where a smooth graph has been drawn through the average position of the points. For convenience values taken from the smooth graph are given in Table III. The probable error of an individual measurement was also calculated from the deviations of measurements made at approximately the same temperature, and amounted to not more than 1%. This showed that the measurements with different tubes are consistent. The probable error of the average found in this way was about 0.3%.

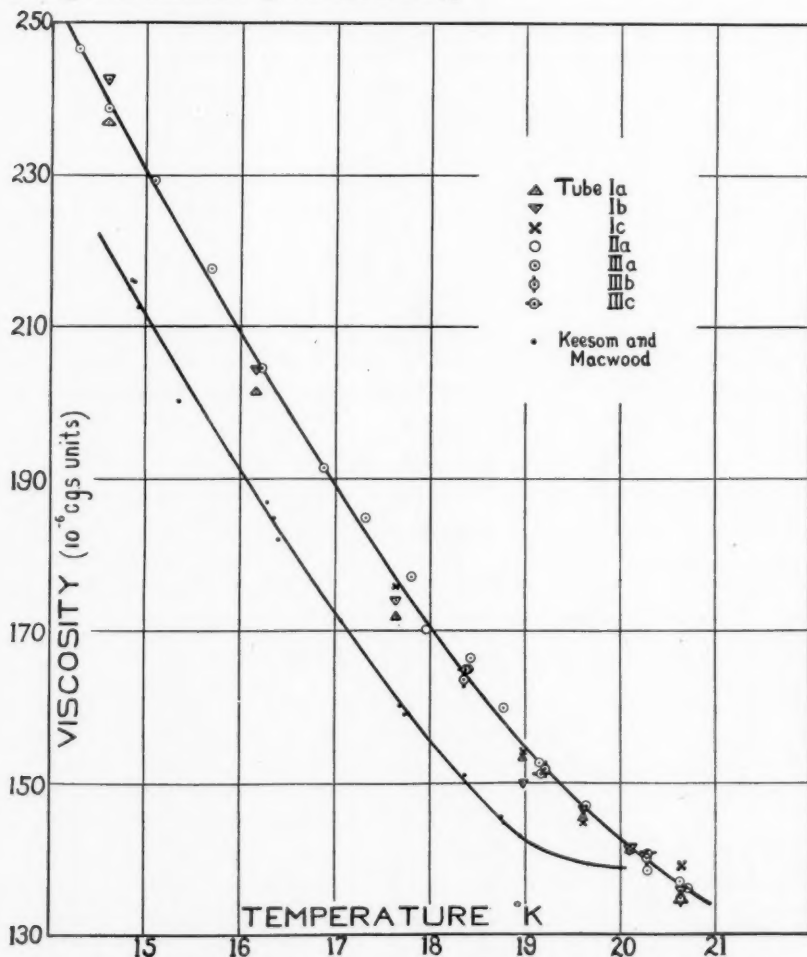


FIG. 2 Relation between the viscosity of liquid hydrogen and the temperature.

For comparison the results of Keesom and Macwood are illustrated graphically in Fig. 2, and smoothed values are given in Table III. It can be seen that the variation with temperature for the two results is approximately the same except for the higher temperatures, but that the results obtained by means of the oscillating disc are about 10% lower than those obtained by the author.

TABLE III  
VALUES OF VISCOSITY ESTIMATED FROM CURVES (FIG. 2)

Temperature, °K.	Viscosity, $10^{-6}$ c.g.s. units	
	Flow method	Oscillating disc
20.6	136.5	
20.41	138.4	
20.0	142.5	138.8
19.0	154.6	142.6
18.0	170.5	155.7
17.0	189.1	172.3
16.0	209.0	191.0
15.0	230.3	211.4
14.5	241.8	

Fig. 3 shows that the relation between  $\log \eta$  and  $1/T$  is linear for the higher temperatures and that the slope  $d \log \eta / d(1/T)$  gradually decreases as the

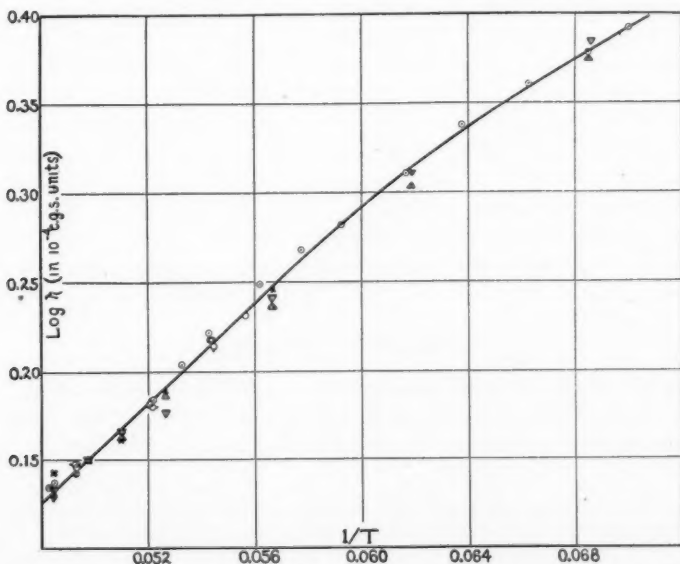


FIG. 3. Relation between the logarithm of the viscosity and the reciprocal of the absolute temperature.

temperature decreases. The linear portion of the graph between  $\log \eta$  and  $1/T$  leads to a viscosity relation of the familiar form

$$\eta = A \exp(E/RT),$$

where the activation energy  $E = 64.6$  cal. per mole. The dependence of the viscosity of liquid hydrogen on temperature is therefore quite normal.

#### Acknowledgments

The author would like to thank Prof. E. F. Burton for his guidance and Prof. H. Grayson Smith and Prof. J. O. Wilhelm for their assistance in this research.

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## EXPERIMENTAL COMPARISON OF SHUNT- AND SERIES-EXCITATION OF A HIGH, UNIFORM CROSS-SECTION, VERTICAL RADIATOR<sup>1</sup>

By K. A. MACKINNON<sup>2</sup>

### Abstract

This paper presents the results of experiments with shunt- and series-excitation of a 0.55 wave, uniform cross-section, vertical radiator. Both unattenuated field strength at one mile and fading characteristics at remote points were determined for each mode of excitation. Whilst Morrison and Smith have already done similar work with a non-uniform cross-section tower, this is the first attempt to examine the fading of a uniform cross-section tower excited in the two modes.

### Introduction

The shunt-excited antenna was introduced by Morrison and Smith (2) in 1936. To check the performance of the design against the ordinary series-excitation method they conducted experiments with the WWJ-Detroit uniform cross-section tower of about 0.38 wave-length physical height for ground-wave efficiency, and with the WSM-Nashville double-tapered tower of 0.58 wave-length for fading characteristics. Their results indicated no substantial difference between the performances of the two modes of excitation.

The fact that the double-tapered type of tower has a current distribution which produces considerably more sky-wave at zenith angles around 30° than does a sinusoidal current distribution (1) suggested the desirability of examining the fading characteristics of a shunt-excited, high, uniform cross-section tower, along which the current distribution when series-excited is approximately sinusoidal. Furthermore, as the WWJ uniform tower is only 0.38 wave-length high it was also considered worth while to compare the ground waves of a high tower using the two modes. The installation of the 50 kw. broadcast transmitter CBF provided an excellent opportunity for these experiments, as it had a shunt-excited uniform cross-section tower of 0.55 wave-length height with an insulated base which of course was short-circuited for shunt-excitation.

### Ground-wave Comparison

The first experiments (February, 1938) were devoted to a comparison of the ground-wave of the CBF tower when shunt-excited with that when series-excited. A low power transmitter of 13 watts was used to excite the tower,

<sup>1</sup> Manuscript received August 22, 1939.

Contribution from the Engineering Division, Canadian Broadcasting Corporation, Montreal, Quebec, Canada. This paper was presented before a joint meeting of the American Section, International Scientific Radio Union and the Institute of Radio Engineers, held at Washington, April 28, 1939.

<sup>2</sup> Transmission and Development Engineer, Canadian Broadcasting Corporation.



and radial field strength measurements were made in various directions over the frozen surface of the St. Lawrence River, beside which CBF is built.

The results indicated that the series-excitation gave about 15% more ground-wave (unattenuated field strength at one mile per kilowatt input) than the shunt-excited. It should be pointed out here however that the power input in the series case was that into the base of the tower, whereas in the shunt case it was the power into the concentric transmission line. Thus the 15% figure should be decreased by an amount dependent on the losses in the line and output terminal equipment. This figure seemed reliable because no absolute values were necessary—the same antenna meter was used at about the same part of the scale in each case, and also the ground-wave was measured along the same radials with the same field strength gear.

The other disturbing feature was the fact that the absolute values found were much too low (212 mv./m./mile/kw. for shunt, 244 for series), whereas figures of the order of 260 should be expected. As a check on this, measurements were repeated with 50 kw. input shunt-excited, and a figure of 224 was obtained. As this was within 6% of the 13 watt shunt measurement, and considering the use of different antenna meters and the great difference in field strengths resulting from the widely different powers, it was felt that the agreement was satisfactory.

The low absolute field of the series-excitation indicated some defect in the ground system. This was further suggested by the much lower figure for shunt-excitation, because it was known that the base current in this mode of operation is much greater than in series-excitation.

No fading comparisons were carried out at this time because of the cold weather.

The following summer, improvements were made to the ground system at the base of the tower and last fall the ground-wave comparison measurements were repeated, using 50 kw. in both cases.

The use of high power in the series-excitation case involved the installation of a two-wire line between the end of the concentric line and the base of the tower with impedance matching equipment at both ends, as well as tower lighting chokes. Fig. 1 indicates the connections and the point where the antenna resistance and current were measured in each case in order to determine the power input. Figs. 2 and 3 give views of the experimental setup at the base of the mast.

The result with the ground system improvements gave a ground-wave for series-excitation of 250 mv./m./mile/kw.; and for shunt-excitation 242, a difference of only 3%. The improvement in per cent due to the ground system changes was thus for series-excitation 250/244 or 2.5% gain, for shunt-excitation 242/212 or 14% gain.

At this point it is interesting to examine the decrease in lumped ground resistance ohms due to the alterations. By inserting an ammeter in the ground strap across the insulated base of the tower it was possible to measure

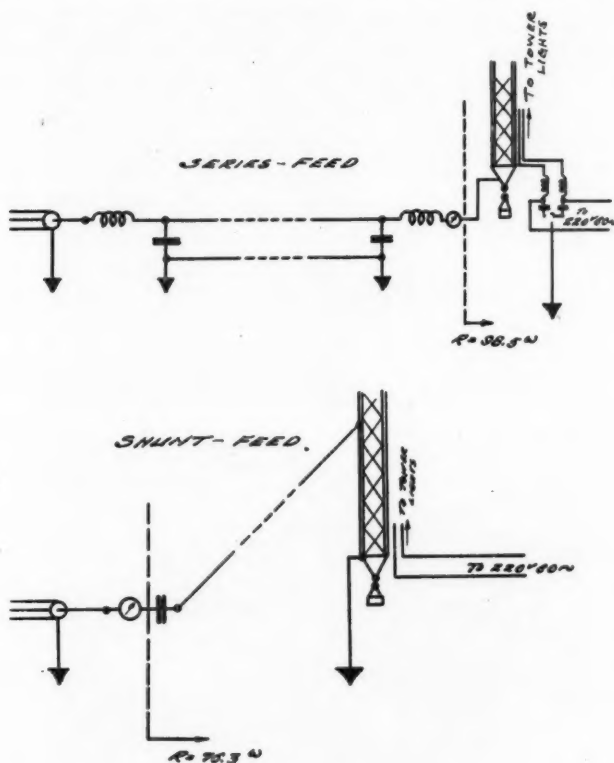


FIG. 1

during shunt-excitation simultaneously both the current in the slanting feed wire and that at the base of the tower. The base current was found to be 2.5 times the current at the bottom end of the feed wire.

These figures permit some simple calculations to be made of the extent of the ground system improvements. For shunt-excitation and 50 kw. into the feed wire (76.3 ohms; see Fig. 1), the feed wire current was 25.6 amp. and thus the base current  $2.5 \times 25.6 = 64$  amp. A 14% loss in ground-wave efficiency means 13 kw. in 50 kw., and thus the ground system changes must have reduced the loss ohms by  $R_1$  where  $(64)^2 R_1 = 13000$  or  $R_1 = 3.2$  ohms.

Similarly, the base current in series-excitation (98.5 ohms; see Fig. 1) was 22.5 amp. A 2.5% loss in efficiency is equivalent to 2.5 kw. in 50 kw., and thus the ground system changes reduced the loss ohms by  $R_2$  where  $(22.5)^2 R_2 = 2500$  or  $R_2 = 4.9$  ohms.

If the radiating system could be considered as actually having a lumped loss resistance it might be expected that  $R_1$  and  $R_2$  would agree more closely. On the other hand, it should be remembered that the change in power loss

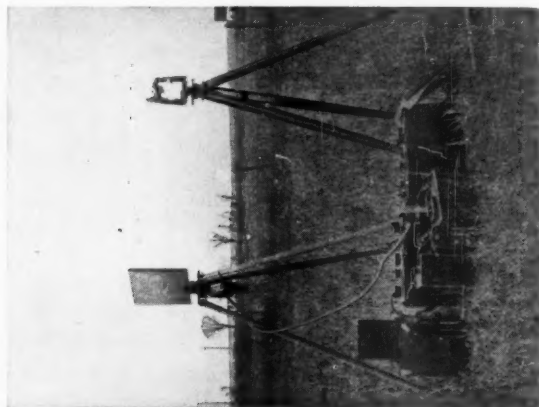


FIG. 4

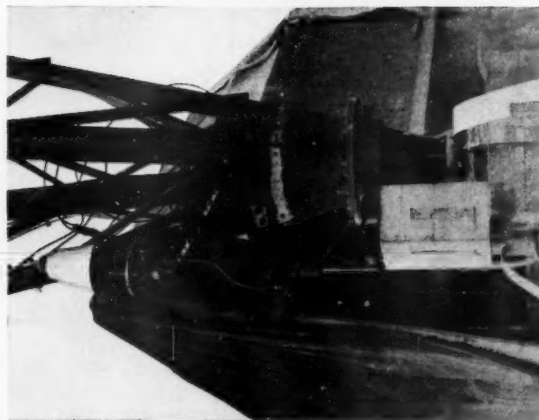


FIG. 3

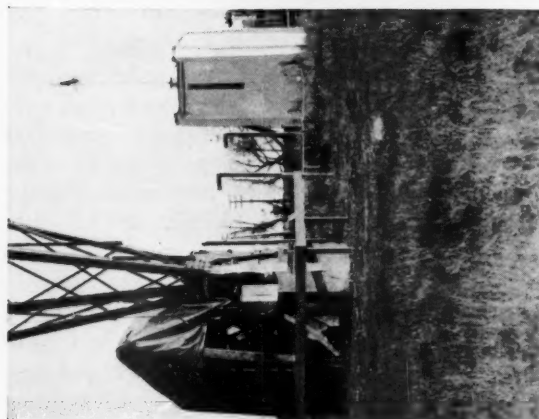


FIG. 2

in these equations has been calculated from field strength measurements. This immediately brings into the picture a number of other unknown factors, such as a possible variation in the polar radiation pattern of the shunt-fed mast due to resistance changes at the mast base causing mismatching of some sort. Nevertheless, this digression indicates the greater need for adequate grounding at the tower base when shunt-excitation is used.

### Discussion of Measuring Methods

There are four factors involved in the determination of ground-wave efficiency (unattenuated field strength at one mile per kw. input to mast); viz.,

- (1) Antenna resistance,
- (2) Antenna current,
- (3) Field strength at given point,
- (4) Linear distance from point to mast.

The procedure adopted to determine each of these will now be discussed in detail.

#### *Antenna Resistance*

This was measured across the base insulator for series-excitation, and between the line terminal of the impedance matching capacity connected to the slanting feed wire and ground for shunt-excitation.

Each resistance was measured by two methods—one using the CBC Antenna Measuring gear which balances two meter readings, and the other using the General Radio R. F. Bridge with its null indication. Each pair of measurements checked within  $\frac{1}{2}\%$ , which was very satisfying, as different operating principles are used in the above instruments.

#### *Antenna Current*

For convenience in changing over from one mode of excitation to the other, a separate antenna meter was used for each connection. In order to check these against each other, they were put in series and compared at the operating frequency (910 kc.), and the ambient temperature (40° F.).

#### *Field Strength*

All the field strength measurements were made with the same Jansky and Bailey instrument with loop on a tripod (see Fig. 4), whose absolute calibration had been checked by the makers some months previously. During the experiments the relative accuracy of the gear over a wide range of field strengths was rechecked.

At all inland points the gear was set up with the tripod. However, at all shore points the gear was set up in a small motorboat, with the tripod feet at water level.

#### *Linear Distance to the Mast*

Linear distance to the mast from the point of measurement was determined by means of a transit. This measured the angular elevation to the top of

the mast, as well as the elevation of the measuring point. The height of the top of the tower and the elevation of its base being known, the distance to the tower could readily be calculated to a much greater accuracy than that of the other three factors required in the ground-wave efficiency determination.

The distances of points more than one mile from the tower were determined by reference to the National Defence map of the area (scale 1 in. = 1 mile). The tower was accurately located thereon by means of azimuth bearings taken on various lighthouses and church steeples visible from CBF.

### Estimated Accuracy

For the relative accuracy, that is the comparison of shunt-excitation ground-wave with that of series-excitation, one should note that:—

- (1) Resistance determinations checked by different methods within  $\frac{1}{2}\%$ ;
- (2) The antenna meters were compared in a series circuit at the operating frequency and temperature, so that the inaccuracies here might be 1% owing to modulation variations;
- (3) The same field strength gear was used throughout;
- (4) The linear distance factor was eliminated by measuring at identical points.

Accordingly, it appears safe to assume a relative accuracy of about 1 or 2% in the ground-wave comparison.

In considering the probable absolute accuracy one has more difficulty in allocating possible errors. The resistance measurement seems likely to be within  $\frac{1}{2}\%$ , as different methods and instruments used gave readings within this value. The antenna meters when compared in a series circuit read within 3% of each other and it is thus probable that the absolute meter error is of half this order. The absolute error of field strength gear is always open to question and in this case one is likely rather optimistic to expect an error of no more than 6% absolute. Linear distance measurement error with the transit was of course of so much higher accuracy than any of the above items that it may be neglected.

Therefore, it appears that the absolute error of the various ground-wave measurements is probably no less than 10%.

### Sky-wave Comparison

The procedure in these sky-wave tests was to operate with 50 kw. into the mast for quarter-hour periods now with shunt-excitation and then with series-excitation. The change-over from one mode to the other was done as rapidly as possible, the time required varying from 10 to 15 min. Time recordings of the resultant field strengths were made simultaneously at various points from 70 to 130 miles from the mast.

The essence of this method of course is to make the change from one mode of excitation to the other rapidly enough to be confident that sky-wave

conditions have not themselves altered in the interval. This state can be assumed if the recordings for at least two consecutive intervals of operation with the same mode are found to be of the same character.

Figs. 5, 6, and 7, of sections of the recordings, show samples of such sky-wave constancy. These are sufficient to indicate that there is no doubt the shunt-excitation method produces much more sky-wave than does the series-excitation. In fact this 0.58 wave tower when shunt-excited behaves from this viewpoint as though it were not much more than half its actual height.

This work was beset with many difficulties, chief of which was the presence on the CBF frequency of a strong Mexican Transmitter, XENT, 150 kw. This interfering station was operating every morning until after daybreak. On most of the nights when strong sky-waves were being received the signal from this station was sufficient to spoil all the recordings. On the other hand, when XENT was weak enough to permit a good recording of CBF, the sky-waves were usually too weak to cause noticeable fading.

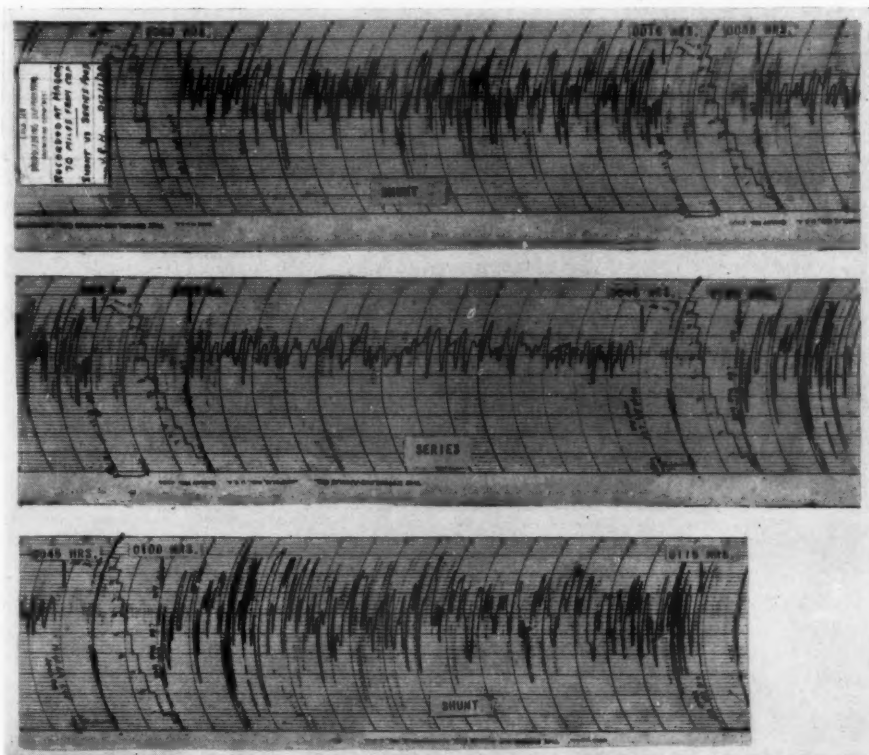


FIG. 5









### Conclusions

To summarize, it may be said that these experiments with the 0.55 wavelength, uniform cross-section tower of CBF have shown that:—

- (1) The ground-wave of this type of tower when shunt-excited can be within 3% of the ground-wave when series-excited, providing that adequate grounding arrangements are made around the tower base;
- (2) The sky-wave suppression when shunt-excited is much less satisfactory than when series-excited.

In the choice between a high mast (say 0.55 wave) and a low mast (0.25 wave) for a high power station there are several factors to be considered:—

- (1) Greater cost of high tower,
- (2) Greater ground-wave efficiency of high tower,
- (3) Greater sky-wave suppression of high tower (when series-excited).

In the basic engineering coverage scheme as announced by the Canadian Broadcasting Corporation, the attainment of a *national* service is considered as the paramount aim. Every extra bit of Canadian territory that gets fading-free service is counted as a gain. Consequently, sky-wave suppression is as important to the CBC as ground-wave efficiency.

There is another aspect to fading which is of importance to the use of our present so-called "clear" channels. The matter of fading is of great moment when strong interfering stations are on the same channel. On 910 kc., for instance, there are CBF—Montreal, 50 kw.; CKY—Winnipeg, 15 kw.; XENT—Nuevo Laredo, 150 kw. Deep fades whether slow or rapid, while readily handled by Automatic Volume Control satisfactorily on clear channels, give poor service on a channel like the above. Each time the signal of CBF fades deeply, XENT bursts in with consequent loss of service. On the other hand, a signal with less fading, such as the records indicate for series-excitation, tends to hold down the interference, thus rendering the service more tolerable.

Accordingly, it is considered that these experiments indicate the unsuitability of shunt-excitation for the high power national outlets of the CBC.

However, for high double-tapered towers, or masts no higher than quarter-wave, it appears that there is little to choose between series- and shunt-excitation from the point of view of ground-wave or sky-wave.

### Acknowledgments

This work was carried out with the able assistance of W. G. Richardson and J. E. Hayes of the CBC Engineering Department. The ready help and co-operation of the CBF transmitter staff were also invaluable. Special thanks are due the Northern Electric Company for the loan of equipment, calibration of meters, and general interest and help given during the experiments.

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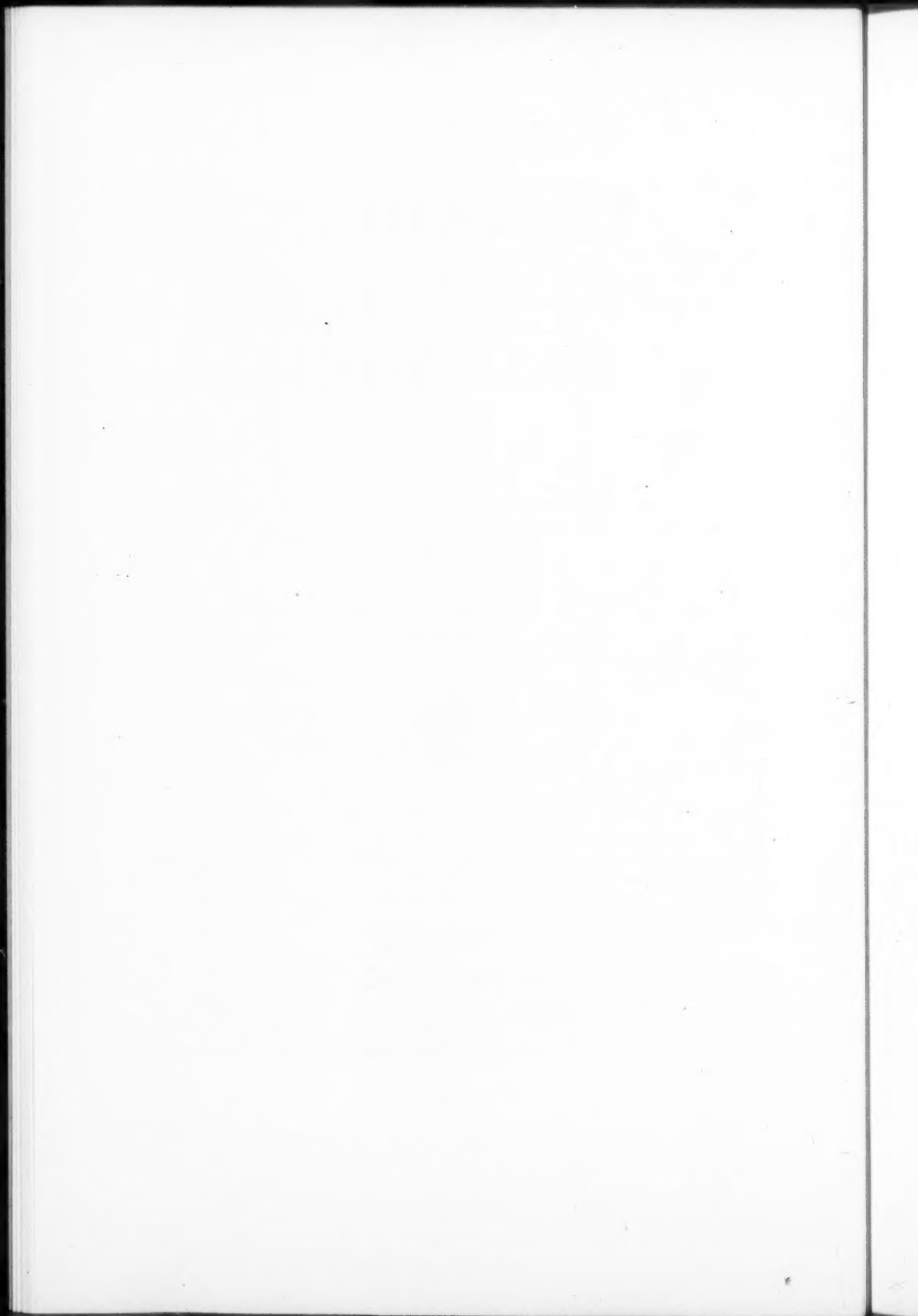
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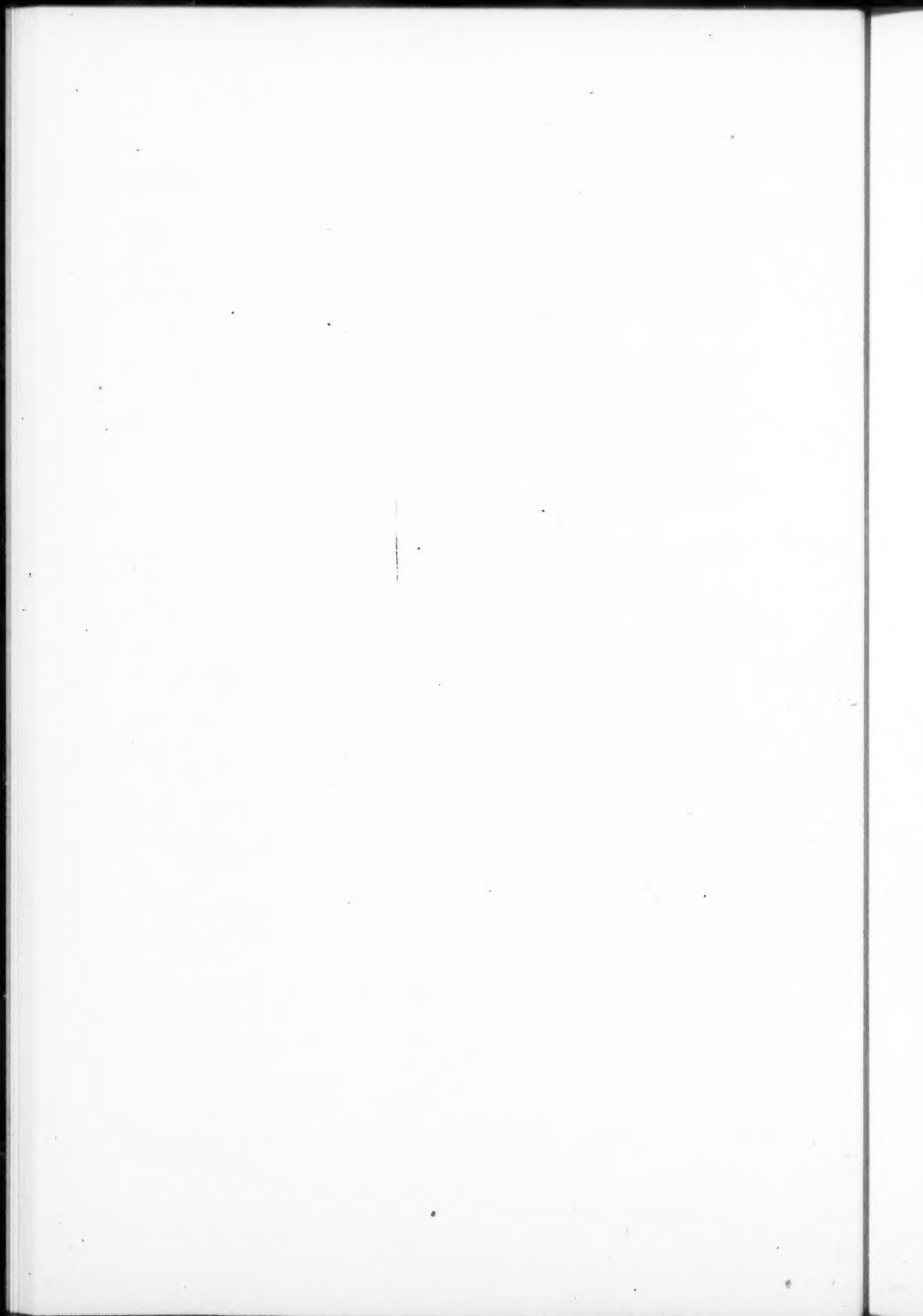
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## THE REACTION OF HYDROGEN AND DEUTERIUM ATOMS WITH PROPANE<sup>1</sup>

BY E. W. R. STEACIE<sup>2</sup> AND N. A. D. PARLEE<sup>3</sup>

### Abstract

The reaction of hydrogen atoms with propane has been investigated over the temperature range 30° to 250° C. by the Wood-Bonhoeffer method. The products are solely methane at low temperatures, and methane, ethane, and ethylene at higher temperatures.

It is concluded that the results can be explained only by the assumption that the reaction



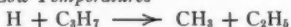
is of importance. The bearing of this on the Rice-Herzfeld mechanisms is discussed. The activation energy of the reaction is  $10 \pm 2$  Kcal.

The main steps in the postulated mechanism are:

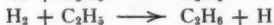
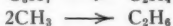
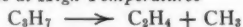
#### Primary Reaction



#### Secondary Reactions at Low Temperatures



#### Additional Secondary Reactions at High Temperatures



The reaction of deuterium atoms with propane was also investigated. It was found that the methane and ethane produced were highly deuterized, while the propane was not appreciably exchanged.

### Introduction

The ethane decomposition has been extensively used as a proving ground for free radical theories [see (18) for references]. The original Rice-Herzfeld mechanism (11) for the ethane decomposition involved as the main steps the reactions:

<sup>1</sup> Manuscript received August 8, 1939.

Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, with financial assistance from the National Research Council of Canada. A preliminary account of some of the work contained in this paper was presented at the Faraday Society Symposium on Hydrocarbon Chemistry, London, April 1939. (21).

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		<i>E</i> , Kcal.
(1)	$C_2H_6 = 2CH_3$	80
(2)	$CH_3 + C_2H_6 = CH_4 + C_2H_5$	20
(3)	$C_2H_5 = C_2H_4 + H$	49
(4)	$H + C_2H_6 = H_2 + C_2H_5$	17
(5)	$H + C_2H_5 = C_2H_4 + H_2$	Small
(6)	$H + C_2H_5 = C_2H_6$	Small

This gives agreement with experiment in so far as the activation energy and the over-all order of the reaction are concerned. Various tests of the scheme have been made by investigating the part reactions. Patat and Sachsse (14, 15) used the ortho-para hydrogen conversion to measure the stationary hydrogen atom concentration in the system, and concluded that it was about 1000 times smaller than that predicted by the Rice-Herzfeld mechanism.

Investigations of the reactions of deuterium atoms with ethane by Steacie and Phillips (22) and by Trenner, Morikawa, and Taylor (28) lead to the conclusion that  $E_4$  is about 8 to 9 Kcal. This removes the disagreement between Patat and Sachsse's results and the Rice-Herzfeld scheme in so far as the hydrogen atom concentration is concerned, but with the new value of  $E_4$  the scheme no longer predicts a first order rate or the correct value of the activation energy of the over-all reaction (23).

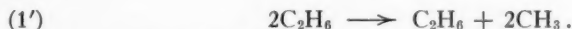
In a recent paper K  chler and Theile (7) have shown that agreement with experiment can still be obtained, *i.e.*, a low H-atom concentration and the proper value of  $E_4$  will still give the correct over-all  $E$  and the first order, if one assumes that the chain breaking process is not (6) but



and that the initial step is bimolecular, *i.e.*, in place of



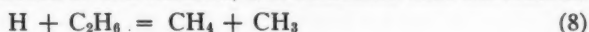
we have



It is thus still *possible* that the ethane decomposition proceeds by a free radical mechanism. Rice and Herzfeld (12) have critically examined and elaborated K  chler and Theile's mechanism. It should perhaps be emphasized that the exactness of the agreement of this scheme (or of any other) with experiment depends to a considerable extent on what value is taken as the over-all experimental activation energy. Estimates from various workers range from 69 to 77 Kcal. On account of difficulties connected with the back reaction and with side reactions, none of these estimates is very reliable, and the over-all activation is probably uncertain to 5 or 6 Kcal. This uncertainty makes it very difficult to make an unequivocal test of proposed mechanisms.

There is, however, a much more serious apparent discrepancy between the Rice theory and experiment which arises from the investigation of the reaction of hydrogen atoms with ethane. Trenner, Morikawa, and Taylor (28) found

that methane was produced in this reaction, and concluded that the reaction

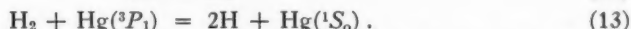


had an activation energy several Kcal. lower than



The production of methane in the reaction of hydrogen atoms with ethane was confirmed by Steacie (17).

Further information about the relative rates of Reactions (4) and (8) comes from the investigation of the mercury photosensitized reactions of ethane (19, 24, 25). Steacie and Phillips concluded that the mechanism of these reactions was:—



This mechanism accounts satisfactorily for the effect of various factors on the process and for the products of the reaction, hydrogen, methane, propane, and butane, provided that it is assumed that Reaction (8) is about four times as fast as (4). This assumption would make still more difficult the application of the Rice theory to the ethane decomposition, since it brings in Reaction (8) as a major step in the process. Actually, however, the occurrence of Reaction (8) would have much more serious consequences than this. All the Rice mechanisms are based on the idea that reactions of the type



occur readily, but that hydrocarbon chain splitting reactions of the type



never occur to an appreciable extent. Hence the ready occurrence of Reaction (8) is contrary to the general postulates of the Rice mechanisms for all substances.\*

In order to account for the production of methane, but at the same time avoid the postulation of chain splitting reactions like (8), Taylor has suggested (26) that methane formation occurs by



This mechanism has received theoretical support from papers by Rice and Teller (13), and Gorin, Kauzmann, Walter, and Eyring (4).

It is apparent from the above discussion that the decision as to the relative probabilities of Reactions (8) and (14) carries with it the fate of practically all the Rice mechanisms. Further information is therefore highly desirable,

and, with this in view, experiments have been made on the reaction of hydrogen atoms with propane.

The only previous work reported on the reactions of H-atoms with propane was two runs made by Trenner, Morikawa, and Taylor (28) who reported that much more methane was formed than ethane, especially at low temperatures.

## Experimental

### *The Reaction of Hydrogen Atoms with Propane*

The reaction was investigated by the Wood-Bonhoeffer method, an electrical discharge being employed to produce atomic hydrogen. The apparatus was similar to that used in previous investigations (16).

Hydrogen was taken from a commercial cylinder, and passed through a quartz tube charged with platinized asbestos and heated electrically to 500° C. The gas then passed through a blow-off trap, through a liquid-air trap to remove water vapour and impurities, and finally gained access to the discharge through a calibrated capillary flowmeter.

Propane was obtained from the Ohio Chemical and Manufacturing Co. The gas contained less than 0.2% of impurities, and was used without further purification. Variations in the flow rate of both hydrogen and propane were accomplished by varying the pressure on the supply side of the capillary flowmeters.

The hydrogen was passed through a U-shaped Pyrex discharge tube of 2.5 cm. bore, about 1 metre long, to which were sealed side tubes containing cylindrical aluminium electrodes. The electrodes were attached to stout platinum wires, which passed out through the glass by means of capillary tubes and de Khotinsky seals. The discharge was operated with an applied voltage of 3500 across the tube and a 5000 ohm resistance. The current was maintained at 200 milliamperes by means of a rheostat in the primary of the transformer.

To obtain maximum efficiency the discharge was situated as close as possible to the reaction vessel. This was a Pyrex cylinder 7 cm. in diameter and 70 cm. long. It was surrounded by an electric furnace which could be slipped up and down the tube to permit observation when the efficiency of the wall poisoning, etc., was being tested. Two tubes entered the reaction vessel from below, one of which contained a thermocouple, while the other served as an inlet for the propane.

The walls of the apparatus were "poisoned" by means of phosphoric acid to prevent recombination of hydrogen atoms. The apparatus was first rinsed out with several litres of distilled water. This was followed by a cleansing rinse with fuming nitric acid, and a further washing with a large quantity of distilled water. The system was then washed out with a 5% solution of phosphoric acid, sealed up, and dried by evacuation through a liquid air trap. This treatment left a coating of metaphosphoric acid on the walls which under higher working temperatures probably dehydrated to phosphoric anhydride.



At any rate the poisoning insured a good working concentration of atoms for some months, providing that the temperatures used were not over 250° C. Above this temperature the anhydride slowly distilled to the colder parts of the apparatus, and the efficiency of the poisoning rapidly diminished.

The hydrogen atom concentration in the reaction vessel was measured by means of a Wrede gauge of the usual type (30). Atom concentration measurements could not, of course, be made by this method in the presence of propane. Measurements were therefore made under nearly identical conditions of pressure, temperature, discharge current, and poisoning. The absence of the propane during these measurements made no great difference in pressure conditions, as the ratio  $H_2/C_3H_8$  was high in most experiments.

The size of the reaction vessel and the speed of the pumps were such that the contact time was of the order of one second. After leaving the reaction vessel the products passed through a liquid air trap which removed propane and higher hydrocarbons, together with most of the ethylene and ethane. The remainder of the gas passed through a high-speed three-stage Leybold mercury diffusion pump. After leaving the diffusion pump the low boiling products were largely removed by a trap containing silica gel maintained at -180° C. The unadsorbed gas passed out through a Hyvac pump. The diameter of all tubing in the pumping and trapping system was about 2 cm., and all stopcocks were of correspondingly large bore.

At the end of a run, which normally lasted about two hours, the traps were allowed to warm up, and the products were pumped into a portable mercury gas holder by means of a Toepler pump. Trials showed that all the ethane and ethylene and virtually all the methane were trapped by the silica gel. A small amount of hydrogen was also retained by the gel.

The products of an average experiment amounted to 500 to 700 cc. Of this a 100 cc. sample was analysed by conventional methods in a Burrell gas analysis apparatus. This was done in order to keep a check on traces of CO, CO<sub>2</sub>, and perhaps C<sub>2</sub>H<sub>2</sub>. The remainder of the products was analysed in a low-temperature distillation apparatus of the Podbielniak type. To prevent "freeze-ups" in the still, water and carbon dioxide were removed by dreierite and soda-lime before the distillation. In the distillation methane and hydrogen were taken off together, and this fraction was analysed by combustion.

### Experimental Results

Sixteen runs were made at four different temperatures. The experimental results are given in Table I.

The results reveal two striking facts: (a) at low temperatures no ethane is produced, (b) no products heavier than propane are found. As these points are of great importance they were checked with considerable care. In the first place synthetic mixtures of H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub> were made up. Distillation analyses on these showed that it would not be possible to miss more than 0.5% ethane, and even this amount could usually be definitely

TABLE I  
REACTION OF HYDROGEN ATOMS WITH PROPANE  
Pressure = 0.36 mm.

Run No.	Temperature, °C.	Atom concentration, %	Propane flow, cc. per sec. at N.T.P.	Hydrogen flow, cc. per sec. at N.T.P.	Products of the reaction, mole per cent					Per cent of C <sub>3</sub> H <sub>8</sub> reacted
					CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	CO <sub>2</sub>	C <sub>2</sub> H <sub>2</sub>	
1	33	22	0.0690	0.517	23.2	0.0	0.0	1.0	75.8	9.60
2	31	22	0.0688	0.539	21.8	0.0	0.0	0.5	77.7	8.70
3	30	22	0.0674	0.521	18.0	0.0	0.7	0.3	81.0	7.55
4	32	22	0.0678	0.521	22.5	0.0	0.0	0.5	77.0	9.10
5	32	22	0.0603	0.515	19.2	0.0	0.0	0.5	80.3	7.60
6	30	22	0.0370	0.507	25.8	0.0	0.0	0.3	73.9	10.55
7	31	22	0.115	0.501	12.8	0.0	0.0	0.3	86.9	4.85
8	100	19	0.0687	0.526	13.5	3.2	0.8	0.5	82.0	8.35
9	100	19	0.0692	0.510	12.5	5.7	0.8	0.5	80.5	9.74
10	172	16	0.0705	0.526	9.7	11.7	1.4	0.6	76.6	13.69
11	171	16	0.0670	0.521	9.2	12.5	2.0	0.6	75.7	14.56
12	170	16	0.0698	0.526	8.8	10.1	1.5	0.6	79.0	12.10
13	170	16	0.0708	0.524	8.8	12.2	1.8	0.6	76.6	13.38
14	250	12	0.0693	0.505	—	—	3.3	0.7	—	—
15	250	12	0.0698	0.524	7.1	14.3	3.2	0.7	74.5	16.06
16	250	12	0.0700	0.524	5.7	14.0	3.2	0.6	76.3	15.09

detected. It may thus be stated with certainty that not more than 0.5% ethane was present in the products of the runs at low temperatures. The absence of hydrocarbons heavier than propane in quantities greater than 0.5% was proved by a few combustion analyses on the last portion of the distillate. A slight oiliness of the mercury in the Toepler pump was discerned after several runs, however, and this leads to the belief that traces of heavier products were present, probably hexane.

Table II gives the collision yield in the various experiments and the activation energies calculated on the assumption that the steric factor  $A$  in the equation

$$\text{Collision yield} = Ae^{-E/RT}$$

is equal to 0.1. In the table  $Z_{\text{C}_3\text{H}_8, \text{H}}$  represents the number of collisions of one propane molecule with hydrogen atoms in the time considered. This is obtained from the relation (6, p. 46).

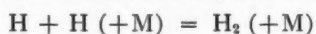
$$Z_{\text{C}_3\text{H}_8, \text{H}} = 2\sqrt{2}\pi \left( \frac{d_{\text{H}} + d_{\text{C}_3\text{H}_8}}{2} \right)^2 \sqrt{\frac{M_{\text{H}} + M_{\text{C}_3\text{H}_8}}{M_{\text{H}} M_{\text{C}_3\text{H}_8}}} \cdot RT \cdot N_{\text{H}},$$

where the  $d$ 's are the molecular diameters, the  $M$ 's the molecular weights, and  $N_{\text{H}}$  is the number of hydrogen atoms per cc. In making the calculation,  $d_{\text{C}_3\text{H}_8}$  taken to be  $4.2 \times 10^{-8}$  cm. (27), and  $d_{\text{H}}$  to be  $2.14 \times 10^{-8}$  (2).

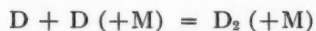
#### The Reaction of Deuterium Atoms with Propane

In the hope that some light might be shed on the nature of the secondary reactions, experiments were also made with deuterium atoms instead of hydrogen atoms.

The apparatus and technique were almost identical with those described in the previous section. The deuterium used was obtained from 99.6% deuterium oxide by treating it with calcium turnings. A slower flow rate was used with deuterium, so as to maintain approximately the same pressure in the apparatus as in the experiments with hydrogen. At the same pressure deuterium will flow through the apparatus more slowly than hydrogen and will thus take more time to get from the discharge to the reaction vessel. During this time, however, it will undergo fewer collisions on account of the lower molecular velocity. These two effects nearly balance and there will be no appreciable difference in the number of collisions undergone by hydrogen or deuterium atoms (or molecules) while travelling between the discharge tube and the reaction vessel. Also, the activation energies of the recombination reactions



and



will not differ appreciably. In view of these considerations there is no appreciable difference in the atom concentration in the two cases, and atom concentration determinations and other tests were made with ordinary hydrogen in order to conserve deuterium. In any case the possible error from this source is negligible compared with the uncertainties in the atom concentration due to fluctuations in the activity of the walls.

TABLE II  
CALCULATION OF COLLISION YIELDS, ETC.

Run No.	Temperature, °C.	Total flow, cc. per sec. at experimental conditions (corrected for presence of atoms)	Reaction time, sec.	Partial pressure of hydrogen atoms, cm.	$Z_{\text{C}_3\text{H}_8, \text{H}}$ per sec.	$Z_{\text{C}_3\text{H}_8, \text{H}}$ in reaction time	Per cent reaction	Collision yield	E, Kcal. assuming $A = 0.1$
1	33	1540	0.890	0.0071	$1.84 \times 10^6$	$1.64 \times 10^6$	9.60	$5.85 \times 10^{-8}$	8.7
2	31	1580	0.868	0.0071	1.85	1.61	8.70	5.40	8.7
3	30	1529	0.895	0.0071	1.85	1.66	7.55	4.55	8.7
4	32	1530	0.895	0.0071	1.85	1.66	9.10	5.50	8.7
5	32	1512	0.907	0.0072	1.87	1.70	7.60	4.45	8.8
6	30	1420	0.965	0.0074	1.92	1.85	10.55	5.70	8.6
7	31	1590	0.861	0.0066	1.72	1.48	4.85	3.30	9.0
8	100	1880	0.729	0.0061	1.44	1.05	8.35	7.95	10.4
9	100	1880	0.729	0.0059	1.39	1.01	9.74	9.65	10.2
10	172	2210	0.620	0.0051	1.10	$6.82 \times 10^5$	13.69	$2.00 \times 10^{-7}$	11.6
11	171	2170	0.631	0.0051	1.10	6.95	14.56	2.10	11.5
12	170	2180	0.628	0.0051	1.10	6.90	12.10	1.75	11.7
13	170	2180	0.628	0.0051	1.10	6.90	13.38	1.95	11.6
14	250	2450	0.559	0.0038	$7.55 \times 10^5$	4.08	—	—	—
15	250	2540	0.540	0.0038	7.55	4.08	16.06	3.95	12.9
16	250	2540	0.540	0.0038	7.55	4.08	15.09	3.70	13.0

In the low temperature experiments, propane was collected in the liquid air trap, and combusted, and the resulting water analysed for deuterium. Methane together with some deuterium was adsorbed by the silica gel trap. Most of the deuterium was separated from the methane by passing the mixture through the distillation apparatus and drawing off the deuterium slowly, using maximum cooling. The remaining methane, containing a little deuterium, was combusted quantitatively and the water analysed for deuterium. The methane generally contained from 1 to 5% of deuterium, for which a correction was made in calculating the extent of deuterization of the methane. In making this correction, the deuterium was assumed to contain no light hydrogen. This assumption introduces no appreciable error, since with about 10% reaction with an 8 to 1 deuterium : propane mixture, the deuterium is over 90% heavy, and there is twice as much (hydrogen + deuterium) in a molecule of methane as in a molecule of "hydrogen", and only 1 to 5% of (hydrogen + deuterium) mixed with the methane. In the runs at higher temperatures where ethane and ethylene were also present, the products were trapped as before, and all pumped off together into a gas-holder. They were then separated by distillation, burned, and the resulting water analysed for deuterium.

Deuterium analyses were made in an apparatus of the Harteck type (5).

The results of the deuterium atom experiments are given in Table III. As methane and propane were the only products of the runs at 30° C., complete separation of the hydrocarbons was simple. The experiments at higher temperatures yielded considerable ethane which was highly deuterized. In Runs 5, 6, and 7 the uncertain end fractions were discarded and only the middle cuts were preserved for analysis. In the distillation apparatus used, the cut between methane and ethane was always quite sharp, but propane and ethane could not be separated so completely. In Runs 5, 6, and 7 the first 30 to 40 cc. of the propane fraction was discarded. The small percentage deuterization of propane in these runs pointed to two possibilities; either the

TABLE III  
REACTION OF DEUTERIUM ATOMS WITH PROPANE

Pressure = 0.35 mm.

Run No.	Temperature, °C.	Atom concentration, %	Propane flow, cc. per sec. at N.T.P.	Deuterium flow, cc. per sec. at N.T.P.	Per cent deuterization of products			
					CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub> uncorrected	C <sub>3</sub> H <sub>8</sub> corrected
1	30	22	0.0690	0.370	—	Absent	<0.5	<0.5
2	30	22	0.0693	0.370	55.0	Absent	<0.5	<0.5
3	30	22	0.0698	0.370	62.3	Absent	<0.5	<0.5
4	30	22	0.0700	0.370	56.5	Absent	<0.5	<0.5
5	170	16	0.0692	0.370	High	52.8	3.4	<0.5
6	170	16	0.0708	0.370	High	65.8	2.5	<0.5
7	250	12	0.0700	0.370	High	54.0	2.2	<0.5
8	250	12	0.0692	0.370	High	—	<0.5	<0.5

propane was exchanged to the extent of about 2.5%, or it was undeuterized but contaminated with a small amount of deutero-ethane from the previous fraction.

To settle this point some highly deuterized ethane was prepared by thermally equilibrating ethylene and excess deuterium. This deutero-ethane was mixed with ordinary propane and distilled. An end fraction of 35 cc. containing ethane and propane was taken as in Runs 5, 6, and 7, and then three successive 35 cc. fractions of propane, *A*, *B*, and *C*. These samples were analysed for deuterium. In Run 8 a similar set of 35 cc. fractions was taken. The detailed results of these deuterium analyses appear below:

Run No.	Per cent deuterization				
	$C_2H_6$	$C_2H_6 + C_3H_8$ end fraction	Fractions of propane		
			<i>A</i>	<i>B</i>	<i>C</i>
Blank	49.0	25.0	7.8	<0.5	<0.5
Run 8	(57.5)	20.1	5.9	<0.5	<0.5

These results prove that the second fraction (*A*) was being contaminated by deutero-ethane, but that further fractions were uncontaminated. It may therefore be concluded that the real deuterization of the propane is less than 0.5%.

Owing to the small yield of methane at the higher temperatures it was found to be very difficult to separate enough of it to give a reliable analysis. Such determinations as were made indicated a high exchange.

### Discussion

It is apparent from the above tables that the main facts in connection with the products of the reaction are:

- Methane is the only detectable product at room temperature.
- At 100° C. ethane is also formed in considerable quantity together with traces of ethylene.
- The amounts of ethane and ethylene increase with increasing temperature.
- Products heavier than propane are not present in detectable quantity.

In Fig. 1 the "collision yields" of the various products have been plotted against temperature. For the purposes of this plot the "collision yield" is defined as the number of molecules of a product formed per collision between a propane molecule and a hydrogen atom. By plotting the results in this manner, they are corrected for the variation in atom concentration with temperature, and for the variation in reaction time with temperature, pressure, etc.

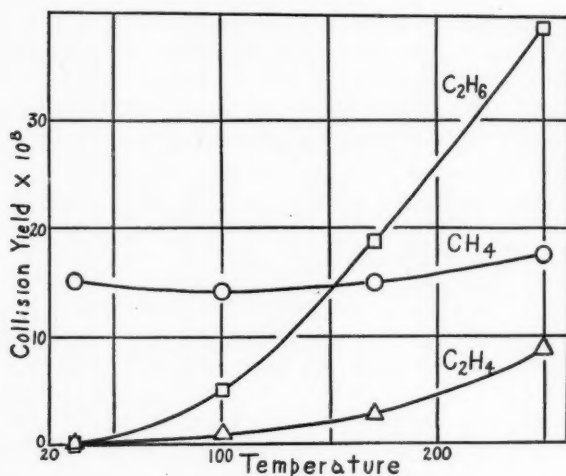


FIG. 1. "Collision yields" of products in the reaction of hydrogen atoms with propane.

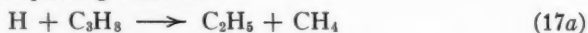
Comparison of the results at room temperature and at 100° C. with the two runs recorded by Trenner, Morikawa, and Taylor shows good general agreement.

#### The Primary Reaction

There are obviously two possibilities for the primary reaction step, the abstraction of a hydrogen atom



or a hydrocarbon chain splitting reaction



Preliminary results on the mercury photosensitized reaction of hydrogen and propane by Steacie and Dewar (20) show that hydrogen and hexanes are the main products, the hexanes undoubtedly being caused by the recombination reaction



This suggests that (16) is the primary step, although the possibility of the occurrence of (17) in the present case cannot be ruled out on this evidence alone.

The non-appearance of hexane in our products is not surprising. In the mercury photosensitized reaction, the pressure is high and the hydrogen-atom concentration is very low. These conditions favour radical recombination reactions, and hexane is therefore to be expected if the propyl radical is present and has an appreciable life. Under the low pressures and high hydrogen concentration (atomic and molecular) of the Wood-Bonhoeffer method, collisions between propyl radicals will be relatively rare and the chance of a

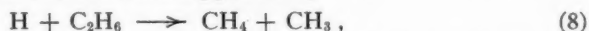


propyl radical reacting with hydrogen will be great. From these considerations the absence of hexane is to be expected, and cannot be offered as an argument against a primary step such as (16).

In general, it may be remarked that there is a very definite parallelism between the reactions of hydrogen atoms with ethane and with propane in so far as a comparison of the results of mercury photosensitization and of the Wood-Bonhoeffer method is concerned. In both cases large amounts of higher paraffins are obtained by mercury photosensitization (propane and butane from ethane, and hexanes from propane) while by the discharge-tube method only lower paraffins are obtained. The difference between the results of the two methods is, of course, due to the difference in the hydrogen-atom concentration and in the pressure.

#### *Secondary Reactions at Low Temperatures*

As stated above, the main feature of the results at 30° C. is the absence of ethane and ethylene in the products and the large production of methane. If the primary step were (17b) the results could not be explained on the assumption that the ethane formed disappeared by



since the apparent activation energy of this reaction is about 7 to 8 Kcal. (17, 28), and hence the reaction of hydrogen atoms with ethane at this temperature is not rapid enough to enable any ethane formed to be completely destroyed. Reaction (17b) may therefore be ruled out as a primary step. In any case (17b) is intrinsically less likely than (17a), since if a C-C bond is to be broken it is much more likely that the bond nearest to the approaching hydrogen atom will split.

If the primary reaction is (17a), then the ethyl radicals produced must react to form methane without the intermediate formation of ethane. The only way in which this can occur seems to be by the reaction

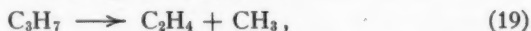


followed by



Taylor has suggested (26) that methane formation in the reaction of hydrogen atoms with ethane occurs by this means, as previously pointed out. The occurrence of reactions such as (14) is also supported on theoretical grounds by the recent work of Gorin, Kauzmann, Walter, and Eyring (4), and by Rice and Teller (13).

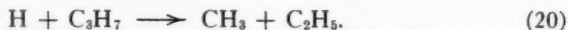
If the primary reaction is (16), then the propyl radicals produced must disappear without the formation of ethane. We cannot postulate appreciable decomposition of the propyl radical by the reaction



since all the evidence indicates that it is stable at room temperature (see Ref. 1). In any case the assumption of Reaction (19) would lead to new difficulties, since it has been shown (29) that the main product of the reaction of hyd-



rogen atoms with ethylene is ethane, and neither ethylene nor ethane occurs as a product at low temperatures. It must therefore be concluded that if the primary reaction is (16) the propyl radicals produced disappear by a reaction analogous to (14), viz.,



If this is the case, then the ethyl radicals formed by (20) must disappear by (14).

It follows that, irrespective of whether the primary reaction is (16) or (17), the results at low temperatures can be accounted for only by the assumption that Reaction (14) occurs readily. The present results therefore furnish strong evidence for the occurrence of (14), and obviate the necessity of assuming reactions of the hydrocarbon chain splitting type like (8). The chain carrying steps in the Rice-Herzfeld mechanisms are therefore left at least qualitatively intact.

#### *Secondary Reactions at Higher Temperatures*

At higher temperatures methane production is diminished, and ethane and ethylene make their appearance. The production of ethylene is undoubtedly to be ascribed to the decomposition of the propyl radical at higher temperatures by Reaction (19). This is in agreement with the fact that the propyl radical can be detected in photodecompositions at ordinary temperatures by the Paneth technique (10), but cannot be detected in thermal decomposition reactions at higher temperatures (9). Bawn (1) estimates an activation energy for Reaction (19) of from 10 to 30 Kcal. The appearance of ethane at higher temperatures is also partly to be ascribed to the reaction



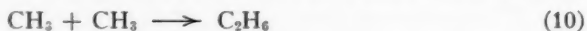
Leermakers (8) estimates an activation energy of 15 Kcal. or more for this reaction, but this estimate is perhaps somewhat high.

The presence of ethylene in the products indicates that the process



must be important as a source of ethane. The ethylene-hydrogen-atom reaction is known to be extremely fast even at room temperature (29), and only a greatly decreased atom concentration can account for the survival of an appreciable amount of ethylene in the products.

Examination of Fig. 1 and Table I shows that at 250° C. the production of ethane is roughly twice that of methane. Each propane molecule broken into must initially yield one mono-carbon and one di-carbon molecule. Hence, if no methyl radical recombination to form ethane occurred, the "collision yield" of methane would be expected to be equal to, or greater than, that of ethane plus ethylene. As this is not the case, ethane must be formed at high temperatures by methyl radical recombination. This will be favoured by high methyl and low hydrogen atom concentration, since the competing processes are



and



At high temperatures the presence of ethylene will lower the hydrogen-atom concentration by consuming hydrogen atoms, and Reaction (10) will therefore increase at the expense of (15). Taylor (26) has previously pointed out that the presence of ethylene serves to reduce the stationary hydrogen atom concentration to very small values.

The evidence that propane does not exchange with deuterium atoms under our experimental conditions makes it unnecessary to include any propane re-forming reactions in the mechanism.

#### *The Activation Energy of the Primary Step*

From Table II it will be seen that the apparent activation energy of the reaction as calculated from the collision yield rises from about 8.7 Kcal. at room temperature to 12 Kcal. at 250° C. This increase is probably not a real one, since the atom concentrations were determined with the Wrede gauge in blank runs, and the presence of ethylene undoubtedly lowers the stationary hydrogen-atom concentration in the runs at higher temperatures. Thus if it were assumed that the atom concentration at 250° C. was only 1% instead of 12%,  $E$  would be lowered from 13 Kcal. to 10.5 Kcal. In view of these uncertainties no very accurate estimate of the activation energy can be made. The most probable value would appear to be about  $10 \pm 2$  Kcal.

Frankenburger and Zell (3) found large decomposition of pentane by hydrogen atoms, which apparently indicated increased reactivity with increasing molecular weight of the hydrocarbon. Our work, however, shows that propane is slightly less reactive to hydrogen atoms than is ethane. This is in agreement with preliminary experiments of Trenner, Morikawa, and Taylor.

There is, of course, the possibility of a propane re-forming reaction. Such reaction would have the effect of increasing the apparent activation energy of the primary step. This possibility was explored by the study of the propane-deuterium reaction, as discussed in the next section.

#### *The Reaction of Deuterium Atoms with Propane*

It will be seen from Table III that in the reaction of deuterium atoms with propane:

- (a) The methane formed is highly deuterized,
- (b) The ethane formed is highly deuterized,
- (c) The unreacted propane is inappreciably exchanged, even at 250° C.

The methane deuterization is higher than can be accounted for by the mechanism previously discussed. This was also the case in the experiments of Trenner, Morikawa, and Taylor (28). It appears likely that the mechanism of this deuterization is that suggested by them, *viz.*, the formation and decomposition of a quasi-methane molecule.



This mechanism was also accepted by Steacie, Alexander, and Phillips (19) to account for the high deuterization of methane formed in the reaction of deuterium atoms with ethane.

The high deuterization of ethane may be partly due to the recombination of highly deuterized methyl radicals to form ethane. It is also probably due to the formation and decomposition of quasi-ethane as previously suggested by Steacie, Alexander, and Phillips,



The propane is inappreciably deuterized. This rules out the possibility of any propane re-forming reaction occurring to an appreciable extent. Reaction (20) must therefore be much faster than the recombination reaction,



under our experimental conditions.

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## A NEW TYPE OF SILICA TANNAGE<sup>1</sup>

BY ALEXANDER ROSE<sup>2</sup>

### Abstract

Silica tannage, usually in combination with other methods, has been extensively investigated, but no process in which silicon compounds were the principal agent has reached the commercial stage.

Ethyl and methyl orthosilicate have been found to possess a marked tanning action when hydrolysed in dehydrated or pretanned pelt. Details of the preparation of silica-tanned leather, analyses and hydrothermal behaviour of the resulting material, and significance of the new method of tannage are discussed.

Silica tannage, alone or in conjunction with every other possible tanning agent from alum to iron and from formaldehyde to zirconium, has been studied and discussed for more than a quarter of a century, but the investigations have usually been empirical in nature. In an early patent Morin (9) described a two-bath tannage, the prepared pelt being first immersed in a solution of an alkali silicate, then in dilute acetic acid, but the resulting leather was not satisfactory. Other investigators suggested the use of colloidal silicic acid or silicates as secondary tanning agents with marked filling properties. Bocciardo and Bocciardo (1) treated formaldehyde-tanned hide with silica sols prepared by neutralization of water glass solutions. Carpmal (2) and others used silicates as precipitants for salts of aluminium, cerium, iron, titanium, or zirconium in the treated pelt. Hough (4, 5) claimed to have developed a satisfactory method of tannage with stabilized silicic acid sols alone, but even in his more exhaustive studies such important data as shrinkage temperatures, resistance to hydrolysis, and aging characteristics have seldom been reported.

The present work, inspired by the more recent writings of Hough (5, 6) and the availability of pure ethyl orthosilicate (supplied by Carbide and Carbon Chemicals Corporation), was at the outset directed toward the development of a white leather that did not possess the shortcomings of the types now on the market, but the remarkable tanning action of the hydrolysis products of alkyl orthosilicates,  $\text{Si}(\text{OR})_4$ , led to studies of a more fundamental character. The preparation, properties, and uses of the orthosilicic esters have received an increasing amount of attention during recent years, and will not be discussed in detail here. From the standpoint of this study the only important property of the lower alkyl orthosilicates is their susceptibility to hydrolysis, particularly by acid solutions.

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### Preliminary Experimental Work

In the earlier experiments the un haired and bated calfskin, washed free of borophenol preservative, was dehydrated in acetone, agitated in pure ethyl silicate for 24 to 72 hr., then transferred to the hydrolysing medium for a like period.

The first sample studied was shaken with ethyl silicate for 24 hr., then with distilled water for the same period, and tacked out while wet. The silica content (dry and oil-free basis) was 32.8%, and the shrinkage temperature was 77° C., as compared with 55 to 60° for the raw calfskin. Shrinkage temperatures were determined by fastening strips of the sample to the bulb of a thermometer and immersing in distilled water; the temperature was raised at a rate of about 5° per min., with constant stirring. The shrinkage temperature was taken as that at which the sample first showed appreciable curling, reduction in area, or, in some cases, the appearance of a distinct groove along the cut edge of the sample.

A second sample was shaken with ethyl silicate for 72 hr., hydrolysed in dilute acetic acid ( $\text{pH} = 3.0$ ) for a further 24 hr., and tacked out while wet. The dried leather was highly plumped, resilient in feel, but rather cracky on the grain even after fat-liquoring. The silica content (dry basis) ranged from 47 to 54%, and the shrinkage temperature from 95 to 100° C., according to the point of sampling. The reduction in area when shrinkage took place was neither rapid nor extensive. Another sample, similarly treated with ethyl silicate, was hydrolysed in distilled water for 48 hr.; it had a silica content of 38 to 43%, and a shrinkage temperature ( $T_g$ ) of 101 to 102° C. in glycerol solution; the grain was very cracky in this case, even after fat-liquoring.

Even more striking was the result when the dehydrated skin was immersed for three days in a mixture of 10% of 20° neat's-foot oil and 90% of ethyl silicate (by weight), and hydrolyzed in distilled water. The  $T_g$  was about 115° in a glycerol solution, but the sample was so stiff and cracky that this figure may be misleading; the silica content was 41.5% on the dry and oil-free basis.

In general, the highest loadings were obtained with samples of pelt from the looser and more open regions of the hide, and in many cases the silica content and shrinkage temperature were considerably lower than those indicated above, owing to poor penetration by the ethyl silicate. Later work was devoted to overcoming the crackiness of grain and non-uniformity of loading which led to the production of unsatisfactory leathers, all of which, however, were pure white when properly fat-liquored.

To overcome the crackiness of grain, as well as the wide variations in silica content which made systematic studies difficult, a number of expedients were tried: hydrolysis in fat-liquors, addition of neat's-foot and mineral oils to the ethyl silicate, vacuum impregnation of the dehydrated pelt after removal of the solvent, and vapour-phase hydrolysis of the silicate in atmospheres saturated with water vapour, sulphur dioxide, or both. The use of sulphur dioxide reduced the time required for hydrolysis from seven days to about



three, for calfskin of normal thickness in saturated water vapour. The natural variations in the porosity of the pelt, together with the hardening or shrinkage of the raw pelt on dehydration with acetone (or, even more so, with methanol), militated against consistent results in this study. After a few experiments, an attempt to follow the progress of the diffusion of ethyl silicate into pelt dehydrated with acetone or methanol was abandoned, the results being highly erratic.

In the course of the work on vapour-phase hydrolysis, one very interesting observation was made. A piece of calfskin, dehydrated with methanol and shaken for three days with a mixture of 85% ethyl silicate, 10% neat's-foot oil and 5% white mineral oil (by weight), was tacked out, grain side up, in the laboratory for three days; the resulting leather was soft, full, resistant to tearing, and had a  $T_g$  of 98° C. with a silica content of 42.3% on the dry and oil-free basis.

In many experiments, including some in which vapour-phase hydrolysis was employed, the grain and flesh surfaces were heavily loaded and the centre of the pelt was obviously undertanned, with resultant low shrinkage temperatures. The more lightly tanned samples, however, were usually superior from the standpoint of resistance to tearing, suppleness, and strength of grain, all of which were low in the heavily loaded leathers, as might be expected.

A small quantity of methyl orthosilicate was synthesized and used in an attempt to increase the average loading and uniformity of results; its tanning properties on hydrolysis were found to be similar to those of the ethyl ester, but no great improvement in the rate of penetration or total loading was noted, despite the higher silicon content of the methyl ester.

### Effect of Various Pretannages

The difficulties experienced in obtaining consistent results by the methods outlined above led to the use of various pretannages as a means of avoiding the inconvenience and detrimental effects (hardening, degreasing, etc.) of the dehydration stage and of keeping the hide in a soft and open condition for the subsequent silica tannage.

Alum tannage, or tawing, was found to be unsuitable; hydrolysis of the silicate in a fat-liquor, for example, removed most of the alumina and gave low fixation of silica and a poor leather, while vapour-phase hydrolysis of the silicate in the tawed pelt resulted in cracky grain and low shrinkage temperatures.

Certain studies by Meunier and Chambard (8) on neutralization of chrome leather with water glass solutions suggested that the colour of a chrome tannage could be masked by a sufficiently heavy loading with silica. The middle split of a commercial sample of chrome upper leather was degreased with acetone and impregnated with ethyl silicate; the original  $T_g$  of 90° C. was reduced to about 80°, probably because of the action of the fat-liquor used for the hydrolysis, and the colour was practically unchanged.

Finally, it was decided that formaldehyde pretannage was the only suitable method. The usual procedure was to drum the bated calfskin for 9 to 12 hr. in about five times its weight of saturated borax solution ( $\text{pH} = 9.1$ ), then add 40% formalin solution in three or four portions over a period of three days until the total amount of formalin solution was 5% on the white weight. The tanned stock was washed thoroughly and tacked out to dry, then lightly fat-liquored and staked. The  $T_g$  was 84 to 86° C. as compared with 60 to 62° for the bated calfskin.

Impregnation with ethyl or methyl silicate and hydrolysis in a fat-liquor did not raise the  $T_g$  of the pretanned material unless the final silica content was 25 to 30% or higher; again, the results were erratic owing to lack of uniformity in the absorption of silicate by the pretanned material. The maximum increase in the  $T_g$  of any sample was about 10° C. Likewise it was found that formaldehyde solutions with pH values between 7 and 8 increased the  $T_g$  of silica-tanned leathers by 5 to 15° in certain cases. The sharp and extensive shrinkage characteristic of formaldehyde-tanned leather persisted after silica tannage.

### Discussion

It would be unwise to indulge in extensive theoretical speculation on the basis of the somewhat scattered results summarized above. There can, however, be no doubt that hydrolysis products of ethyl and methyl silicate have, under appropriate conditions, a true tanning action, the mechanism of which is a matter for future elucidation. Under the conditions of hydrolysis employed in the present work the state of molecular aggregation and chemical reactivity of the silica formed, together with its proximity to the protein fibrils at the moment of formation, would lead to a type of combination markedly different from that obtained by tannage with so-called "colloidal silicic acid", prepared by neutralization and stabilization of solutions of alkali silicates, or by acidification of hides previously treated with water glass solutions.

Hurd (7) has pointed out in a recent review that hydrated silicic acid when first formed by acidification of alkali silicate solutions may have a molecular weight corresponding roughly to the monomeric condition, that in this state it may pass readily through the usual types of dialysing membranes; and condenses rapidly to complexes of very high molecular weight. If an active group in such a complex should react with active groups in the protein chains, the marked tanning action of the freshly formed silica would not be surprising. Hough (5) has stated that silica tannage may be conveniently combined with formaldehyde tannage but does not improve vegetable-tanned leather; he suggested that the vegetable tannins and silicic acid probably combined with the same groups in the collagen structure. The small increase in shrinkage temperature when formaldehyde-tanned leather is given a subsequent silica tannage points to a similar explanation, since it is generally agreed that formaldehyde tannage takes place at the amino and imino groups. If the silica does combine with these basic groups, then the pH of the hydrolysing medium



would probably affect the rate and effectiveness of the tannage, as well as the rate of hydrolysis of the orthosilicate ester. On the other hand, the tanning properties may be due to purely physical protection of the protein chains by strongly adsorbed layers of silicic acid micelles.

While the tannage described is hardly of commercial importance under present conditions, the tanning properties of the hydrolysis products of the alkyl orthosilicates deserve further study. The difficulties described in the present paper might be overcome to a certain extent by the use of carefully graded hide powder as raw material. Quantitative hydrolysis studies by the method of Gerngross and Gorges (3) on hide powder tanned with silica, formaldehyde-silica, or chrome-silica; X-ray spectrographic studies; investigation of the effects of various conditions (pH, temperature, etc.) during hydrolysis of the silicate; tannage with silica produced by hydrolysis externally as well as *in situ*; studies of the rate of hydrolysis of the orthosilicic esters and the state of aggregation of the resulting products;—these and other experimental approaches suggest themselves. The results may throw some light on the mechanism of tanning in general, and of formaldehyde and vegetable tanning in particular, which will justify the effort involved.

#### Acknowledgment

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## STUDIES IN ISOUREAS AND ISOUREIDES

V. THE ADDITION OF DIHYDRIC AND SUBSTITUTED ALCOHOLS TO CYANAMIDE<sup>1</sup>BY S. BASTERFIELD<sup>2</sup>, F. B. S. RODMAN,<sup>3</sup> AND J. W. TOMECKO<sup>4</sup>

## Abstract

In continuation of earlier studies on the formation of alkyl-isoureas by the addition of alcohols to cyanamide, a series of new isoureas has been prepared from ethylene glycol, glycol mono-ethyl ether, glycol mono-acetate, ethyl glycollate, ethanolamine, and resorcinol. In addition, the preparation of allyl-isourea, which had previously failed, *m*-nitrobenzyl- and cyclohexyl-isoureas was accomplished. The new isoureas were characterized by the preparation of salts (salicylates or benzoates), and of cyclic isoureides by condensation with acetoacetic and malonic esters. Some further study was made of benzyl- and phenylethyl-isoureas, previously prepared in this laboratory.

In an earlier study (2), it was shown that the formation of isoureas, by the addition of anhydrous alcohols to cyanamide in the presence of hydrogen chloride, generally takes place readily at room temperature. The rate of addition was found to vary considerably with the nature of the alcohol, the time of disappearance of the reaction for free cyanamide ranging from 24 hr. for methyl and ethyl alcohols, to seven to eight days for benzyl and phenylethyl alcohols. Unexpectedly, allyl alcohol appeared to react very slowly, and from the dark-coloured residue obtained after long standing, no isourea was isolated. In the present study, carefully purified allyl alcohol was found to react quite smoothly with cyanamide, with the production of allyl-isourea in good yield. It is apparent that some unknown impurity was responsible for inhibiting the addition reaction in the earlier investigation.

In the present investigation a new series of isoureas has been prepared by the addition to cyanamide of the following alcohols: ethylene glycol, glycol mono-ethyl ether, glycol mono-acetate, ethyl glycollate, ethanolamine, and *m*-nitrobenzyl alcohol. In addition the preparation of cyclohexyl-isourea (previously recorded (1) ) is described and further study of benzyl- and phenylethyl-isoureas reported.

The experiments reported in this paper show that while ethylene glycol reacts with cyanamide with a speed comparable to that of the simple monohydric alcohols, the glycol ether and acetate are far less reactive, and seem to fall into a group with ethyl glycollate and resorcinol. Ethanolamine is

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remarkable for its extraordinarily low speed of reaction. It is an exceptional case in that two equivalents of hydrogen chloride are required for the reaction, the basic group of the alcohol absorbing one equivalent. Although  $\beta$ - $\beta'$ -dihydroxy-ethyl ether appeared to react almost as fast as the simple alcohols, no isourea was obtained from the reaction. The reaction has not been examined further.

TABLE I  
ADDITION OF ALCOHOLS TO CYANAMIDE

Alcohol	Time of disappearance of cyanamide		Molar ratio alcohol/cyanamide	Solvent
	20-22° C.	40° C.		
Methyl	24 hr.	18 hr.	12 : 1	Reacting alcohol
Ethyl	26 hr.	23 hr.	12 : 1	Reacting alcohol
Allyl	5 days	22 hr.	12 : 1	Reacting alcohol
Cyclohexyl	24 hr.	—	12 : 1	Reacting alcohol
Glycol mono-ethyl ether	18 days	5 days	12 : 1	Reacting alcohol
Ethylene glycol	41 hr.	18 hr.	1 : 1	Ethylene chlorhydrin
Glycol mono-acetate	36 days	5 days (+)	1 : 1	Ethylene chlorhydrin
Ethyl glycollate	20 days	5 days	1 : 1	Ethylene chlorhydrin
Resorcinol	23 days	5 days (-)	1 : 1	Ethylene chlorhydrin
Ethanolamine	12 months	7 months	1 : 1	Ethylene chlorhydrin

The rates at 40° C. are more significant for comparison since, at room temperature, a precipitate of cyanamide dihydrochloride was often formed when hydrogen chloride was added, and the amount of the former varied with different alcohols as did also the rate at which it disappeared. An excess of hydrogen chloride above the required equivalent definitely reduced the rate of addition. In one preparation of ethyl-isourea, two equivalents of hydrogen chloride were added in error, and the reaction for cyanamide disappeared only after a week had elapsed. The effect of excess hydrogen chloride was confirmed by other experiments. On the assumption that free alcohol is the reactant, this effect may be due to the combination of alcohol with hydrogen chloride to form the oxonium salt, which decreases the concentration of free alcohol. This may be true despite the fact that the reaction does not proceed at all in the absence of hydrogen halide. The influence of increased concentration of alcohol was readily apparent when larger molar ratios of alcohol to cyanamide than 12 : 1 were used. With methyl and ethyl alcohols, the excess of which could be readily removed, the reaction time was reduced to about 12 hr. at room temperature, and with very pure cyclohexanol to about 14 hr.

It is interesting to observe that both ethylene glycol and resorcinol yielded only mono-isoureas; in other words, only one hydroxyl group functioned.

If di-isoureas were formed they were not present in sufficient quantity to be isolated.

Benzyl- and phenylethyl-isoureas were prepared in the previous study (2), but because of the smallness of the yields and the fact that only the salicylates were analyzed, it was thought desirable to repeat the work and characterize these isoureas further by means of condensation products. The salicylate of phenylethyl-isourea was found to melt at 158° C. as compared with 134° C. recorded by Basterfield and Powell (2). The analysis for nitrogen also gave figures closer to the calculated result than did the analysis of the earlier product. (Calcd.: N, 9.27%. Found: N, 9.33, 9.24%. Previous analysis:—found: 8.94, 8.94%). Samples of both the older and newer preparations were examined microscopically. The older material contained amorphous masses and the crystals were poorly defined. The newer material consisted of well defined rectangular crystals and was free from amorphous particles. The older material was carefully recrystallized from alcohol until it was free of amorphous material, and the crystals were of good form. The melting point was then found to be 158° C.,† identical with that of the newer preparation.

In the preparation of the isourea hydrochloride the general method was modified to suit the type of alcohol employed. When the alcohol was sufficiently volatile to be distilled under reduced pressure at a moderately low temperature, it was used as the medium for the reaction, and the excess was removed by distillation when the addition reaction was complete. For less volatile alcohols, equimolecular proportions of alcohol and cyanamide were dissolved in ethylene chlorhydrin (10 to 12 moles) which does not react with cyanamide. The isourea hydrochloride was precipitated by pouring the reaction residue into ice cold ether, after most of the solvent had been removed by distillation at low pressure.

The free bases were liberated from the crude hydrochlorides, which were oils or semicrystalline masses, by treatment with powdered sodium or potassium hydroxide in contact with moist ether. Since some of the bases were unstable and their ether solutions became turbid from the separation of polymerized decomposition products, the ether solutions were filtered rapidly into an ether solution of salicylic or benzoic acid. The salicylates or benzoates usually separated rapidly. They were filtered off and recrystallized from alcohol. The more stable bases were obtained from the ether solutions as oils or low melting point solids and mixed with the required amount of acetoacetic or malonic ester to give the cyclic isoureides. These were formed at room temperatures when the reaction mixtures were allowed to stand in a desiccator for a few hours. All barbituric acid ethers were confirmed by being converted to barbituric acid.

†Melting points are uncorrected.

### Experimental

#### I. Allyl-isourea and Derivatives

##### (1) Allyl-isourea Hydrochloride. $\text{H}_2\text{N} \cdot \text{C}(\text{OCH}_2\text{CH} : \text{CH}_2) : \text{NH}_2\text{Cl}^+ \text{ } ^-$

The salt was obtained as a hygroscopic crystalline solid below room temperature. At room temperature it rapidly melted to an oil. The free base obtained from it by the method described in the introduction was an unstable colourless oil with an odour of allyl alcohol.

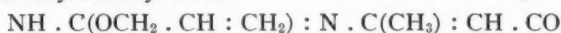
##### (2) Allyl-isourea Salicylate

When the free base in ether solution was mixed with an equivalent of salicylic acid in ether, the salt was obtained in glistening white flakes; m.p., 126° C. Calcd. for  $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_4$ : N, 11.76%. Found: N, 11.50, 11.71%.

##### (3) Allyl-isourea Benzoate

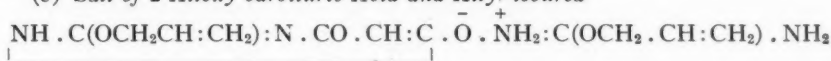
White needles; m.p., 148° C. Calcd. for  $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_3$ : N, 12.61%. Found: N, 12.56, 12.42%.

##### (4) 2-Alloxy-4-methyl-uracil



The isoureide was obtained as a white solid when equivalent quantities of the base and ethyl acetoacetate were mixed without a solvent and allowed to stand in a desiccator. It crystallized from benzene in long flat needles; m.p., 164°. Yield, 90%. Calcd. for  $\text{C}_8\text{H}_{10}\text{N}_2\text{O}_2$ : N, 16.86%. Found: N, 16.75, 16.70%.

##### (5) Salt of 2-Alloxy-barbituric Acid and Allyl-isourea



The salt was obtained when allyl-isourea was mixed with a slight excess of methyl malonate and the mixture allowed to stand in a desiccator for some hours. It was recrystallized from a mixture of methyl alcohol and ether; m.p., 149 to 150° C. Yield, 60%. Calcd. for  $\text{C}_{11}\text{H}_{16}\text{N}_4\text{O}_4$ : N, 20.90%. Found: N, 21.01, 21.24%.

##### (6) 2-Alloxy-barbituric Acid

The acid was liberated from its salt by the action of dilute hydrochloric acid. It was recrystallized from hot alcohol; m.p., 171°. Yield, quantitative. Calcd. for  $\text{C}_7\text{H}_8\text{N}_2\text{O}_3$ : N, 16.67%. Found: N, 16.35, 16.51%. It was converted to barbituric acid by heating with hydrochloric acid.

#### II. Cyclohexyl-isourea and Derivatives

##### (1) Cyclohexyl-isourea Hydrochloride. $\text{H}_2\text{N} \cdot \text{C}(\text{OC}_6\text{H}_{11}) : \text{NH}_2\text{Cl}^+ \text{ } ^-$

The salt was obtained as a white granular hygroscopic solid. It was recrystallized from ethyl alcohol; m.p., 168°. Yield, 90%. Calcd. for

\*The formulae of isourea salts all indicate the ammonium ion formed by absorption of the proton at the imino-group. In previous papers, the formulae showed the ion formed at the amino-group. The change has been made to conform to the findings of Lecher and his associates on the structure of the guanidinium ion and of thiourea as a zwitter-ion.

$C_7H_{14}ON_2 \cdot HCl$ : N, 15.72%. Found: N, 15.64%. The free base was obtained as a greasy white solid; m.p., 77 to 78°.

(2) *Cyclohexyl-isourea Salicylate*

Glistening flakes very soluble in alcohol, but rather insoluble in ether, chloroform, or ligroin; m.p., 153°. Calcd. for  $C_{14}H_{20}N_2O_4$ : N, 10.00%. Found: N, 9.84, 9.73%.

(3) *2-Cyclohexoxy-4-methyl-uracil*

The preparation of this isourea was similar to that of the allyl compound. It formed white flaky crystals from a mixture of benzene and ligroin. It was very soluble in alcohol; m.p., 110°. Yield, 50%. Calcd. for  $C_{11}H_{16}N_2O_2$ : N, 13.46%. Found: N, 13.33, 13.25%.

(4) *Salt of 2-Cyclohexoxy-barbituric Acid and Cyclohexyl-isourea*

(See formula of allyl compound for type structure.)

The compound was obtained by crystallization from ethyl alcohol as a fine white powder; m.p., 190° C. Yield, 60%. Calcd. for  $C_{17}H_{28}N_4O_4$ : N, 15.91%. Found: N, 15.77, 15.82%.

(5) *2-Cyclohexoxy-barbituric Acid*

The acid was liberated from its salt by means of dilute hydrochloric acid, and recrystallized from alcohol. White powder; m.p., 240° C. Yield, 70%. Calcd. for  $C_{10}H_{14}N_2O_3$ : N, 13.32%. Found: N, 13.13, 13.21%.

III. *Benzyl-isourea and Derivatives*

(1) Benzyl-isourea hydrochloride obtained as a semicrystalline mass was converted into the free base and neutralized with an ether solution of salicylic acid. The salt was recrystallized from alcohol and found to melt at 140° C. as previously recorded by Basterfield and Powell (2).

(2) *2-Benzoxyl-4-methyl-uracil*

Equimolecular quantities of the base and ethyl acetoacetate were mixed and allowed to stand over concentrated sulphuric acid for some hours. The solid formed was recrystallized from alcohol. It melted at 153° C. with decomposition. Analysis showed that the compound was not the simple uracil ether as obtained in other cases, but a product involving a second molecule of benzyl-isourea. The nitrogen content found was 16.09, 16.03%, which agrees with the nitrogen calculated for  $C_{20}H_{20}N_4O_2$  (16.11%), a compound which could be formed from one molecule of the benzoxy-methyl-uracil and one of benzyl-isourea with elimination of one molecule of water. The substance was decomposed by dilute hydrochloric acid, with the precipitation of the expected uracil; m.p., 160° C. Calcd. for  $C_{12}H_{12}N_2O_2$ : N, 12.9%. Found: N, 12.6%.

IV. *m-Nitrobenzyl-isourea and Salts*

(1) *m*-Nitrobenzyl-isourea hydrochloride was obtained in small yield as a semisolid mass. The reaction was carried out in ethylene chlorhydrin and the reaction for cyanamide disappeared in seven days.



(2) *m*-Nitrobenzyl-isourea Salicylate

The free base was liberated from the crude hydrochloride into ether, and the solution neutralized with salicylic acid. The salt was precipitated immediately and was recrystallized from alcohol; m.p., 137° C. The yield was only 7% of the theoretical. Calcd. for  $C_{18}H_{18}N_3O_6$ : N, 12.3%. Found: N, 12.1, 12.1%.

V. Phenylethyl-isourea and Derivatives

(1) Phenylethyl-isourea Salicylate

The salt formed by the usual procedure was crystallized from alcohol; it melted at 158° C. Calcd. for  $C_{16}H_{18}N_2O_4$ : N, 9.27%. Found: N, 9.33, 9.24%.

(2) 2-Phenylethoxy-4-methyl-uracil (?)

The preparation of this compound was similar to that of the benzyl compound. The solid after recrystallization from alcohol melted at 178° C. Yield, about 40%. The product was accidentally lost before an analysis was made.

VI.  $\beta$ -Hydroxyethyl-isourea Salts

(1)  $\beta$ -Hydroxyethyl-isourea Hydrochloride.  $H_2NC(OCH_2 \cdot CH_2OH) : NH_2Cl$

In the first preparations cyanamide was dissolved in ethylene glycol, and the calculated amount of dry hydrogen chloride passed into solution. When the reaction for cyanamide had disappeared, the excess of glycol was removed by vacuum distillation and the residue was poured into ice cold ether. The white solid obtained was not the expected hydrochloride and yielded no base by the usual procedure. When the procedure was modified by pouring the whole reaction mixture into ether without previous distillation of excess glycol, the precipitated solid yielded a small amount of the expected isourea when suitably treated.

A much better result was obtained by dissolving equimolecular quantities of cyanamide and glycol in ethylene chlorhydrin and treating the solution with the required amount of hydrogen chloride. The reaction mixture was poured into cold ether, and the isourea hydrochloride was precipitated as an oil which solidified at -12° C. At room temperature it formed an oily mush of crystals.

(2)  $\beta$ -Hydroxyethyl-isourea Salicylate and Benzoate

The impure hydrochloride was converted to the free base in the usual way, and the ether solution of the latter mixed with an ether solution of salicylic acid. The salt appeared in silky flakes; m.p., 141.5° C. Calcd. for  $C_{10}H_{14}N_2O_6$ : N, 11.56%. Found: N, 11.32, 11.37%.

The benzoate was obtained in a similar manner, as a mass of fine hair-like crystals; m.p., 134° C. Calcd. for  $C_{10}H_{14}N_2O_4$ : N, 12.39%. Found: N, 12.25, 12.30%.



VII.  *$\beta$ -Ethoxy-ethyl-isourea Salts and Derivatives*

(1)  *$\beta$ -Ethoxy-ethyl-isourea Hydrochloride.*  $\text{H}_2\text{N}^+\text{C}(\text{OCH}_2\text{CH}_2\text{OC}_2\text{H}_5) : \text{NH}_2^-\text{Cl}^-$ .

A mixture of cyanamide and glycol mono-ethyl ether was treated with hydrogen chloride. The reaction for the preparation of this compound was carried out with an excess of the alcohol itself as the solvent. The hydrochloride was obtained as a reddish mush of crystals, which was converted in the usual way to the free base. The latter was a colourless oil, which slowly deposited crystals of high melting point.

(2)  *$\beta$ -Ethoxy-ethyl-isourea Salicylate*

Two grams of the oil dissolved in ether was neutralized with an equivalent of salicylic acid in ether. The salt separated in flaky crystals; m.p.,  $101^\circ$  to  $102^\circ$  C. Yield, almost quantitative. Calcd. for  $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_5$ : N, 10.40%. Found: N, 10.27, 10.34%.

(3) *2-( $\beta$ -Ethoxy-ethoxy)-4-methyl-uracil*

The isourea was mixed with its molecular equivalent of ethyl acetoacetate and allowed to stand in a desiccator. The solid obtained was recrystallized from benzene. It gave fine white needles; m.p.,  $121^\circ$  C. Yield, about 50%. Calcd. for  $\text{C}_9\text{H}_{14}\text{N}_2\text{O}_3$ : N, 13.08%. Found: N, 13.20, 13.40%.

(4) *Salt of  $\beta$ -Ethoxy-ethyl-isourea and 2-( $\beta$ -Ethoxy-ethoxy)-barbituric Acid*

The isourea was mixed with one equivalent of methyl malonate and allowed to stand. The solid was recrystallized from alcohol. It gave white granular crystals; m.p.,  $158^\circ$  to  $159^\circ$ . Yield, about 50%. Calcd. for  $\text{C}_{13}\text{H}_{24}\text{N}_4\text{O}_6$ : N, 16.92%. Found: N, 16.99, 17.10%.

(5) *2-( $\beta$ -Ethoxy-ethoxy)-barbituric Acid*

The compound was immediately precipitated when the above salt was treated with dilute hydrochloric acid. It was recrystallized from alcohol; m.p.,  $138^\circ$ . Calcd. for  $\text{C}_8\text{H}_{12}\text{N}_2\text{O}_4$ : N, 14.00%. Found: N, 14.10, 14.21%. The substance was converted into barbituric acid by the action of hot hydrochloric acid.

VIII.  *$\beta$ -Amino-ethyl-isourea Salts*

(1)  *$\beta$ -Amino-ethyl-isourea Dihydrochloride.*  $\text{NH}_2\text{C}(\text{OCH}_2\text{CH}_2\text{NH}_3^+\text{Cl}^-) : \text{NH}_2^+\text{Cl}^-$

Equivalent quantities of cyanamide and ethanolamine were dissolved in ethylene chlorhydrin and two molecular equivalents of gaseous hydrogen chloride passed into the solution. The reaction proceeded for several months. When the reaction was complete the mixture was poured into cold ether, whereupon the hydrochloride was precipitated as a light yellow oil which darkened on standing. It was converted at once to the disalicylate.

(2) *Disalicylate.*  $\text{NH}_2\text{C}(\text{OCH}_2\text{CH}_2\text{NH}_3^+\text{OOC}\cdot\text{C}_6\text{H}_4\text{OH}) : \text{NH}_2^+\text{OOC}\cdot\text{C}_6\text{H}_4\text{OH}$

The oil was treated in the usual way, the free base being liberated into ether and neutralized with salicylic acid. The disalicylate was precipitated as white silky flakes; m.p., 141.5°. Calcd. for  $C_{17}H_{21}N_3O_7$ : N, 11.08%. Found: N, 10.81, 10.87%.

(3) *Dibenzoate*. Prepared as above for the salicylate. The salt was precipitated as a bulky white powder; m.p., 123°. Calcd. for  $C_{17}H_{21}N_3O_5$ : N, 12.01%. Found: N, 11.91, 11.98%.

#### IX. $\beta$ -Acetoxyethyl-isourea Salts

(1) Purified ethylene glycol mono-acetate and cyanamide were dissolved in equimolecular proportions in ethylene chlorhydrin. The hydrochloride of the isourea was obtained as colourless oil.

(2) The free base was liberated into ether and was apparently unstable. The ether solution became cloudy from the separation of polymerized decomposition products and was filtered rapidly into ether solutions of salicylic and benzoic acids.

The salicylate,  $NH_2 \cdot C(OCH_2CH_2O \cdot COCH_3) NH_2 \cdot OOC \cdot C_6H_4OH$ , was obtained as silky white flakes; m.p., 138°. Calcd. for  $C_{12}H_{16}N_2O_6$ : N, 9.86%. Found: N, 10.11, 10.20%. The benzoate appeared as masses of fine, hair-like needles; m.p., 129°. Calcd. for  $C_{12}H_{16}N_2O_5$ : N, 10.45%. Found: N, 10.65, 10.75%.

#### X. Carbethoxy-methyl-isourea Salts

(1) *Carbethoxy-methyl-isourea Hydrochloride*.  $NH_2 \cdot C(OCH_2 \cdot COOC_2H_5) : NH_2Cl$

Ethyl glycollate and cyanamide dissolved in ethylene chlorhydrin and treated with anhydrous hydrogen chloride gave the isourea hydrochloride as a colourless oil.

(2) The free base liberated into moist ether by the action of potash was apparently hydrolyzed with the loss of the ester group since the salts obtained from it were not *carbethoxy* but *carboxy* isourea salts.

*Carboxy-methyl-isourea Salicylate*.  $NH_2 \cdot C(OCH_2 \cdot COOH) : NH_2 \cdot OOC \cdot C_6H_4OH$

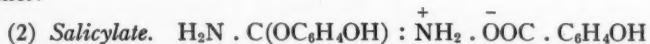
The free base liberated into ether and neutralized with salicylic acid gave a salt crystallizing in white glistening flakes from alcohol; m.p., 136°. Calcd. for  $C_{10}H_{12}N_2O_6$ : N, 10.93%. Found: N, 10.87, 10.69%.

*Benzoate*. This salt was obtained as a fine powder which crystallized from alcohol in silky needles; m.p., 124°. Calcd. for  $C_{10}H_{12}N_2O_5$ : N, 11.24%. Found: N, 11.33, 11.36%. It was observed that the ether solution of the free base rapidly became cloudy before it could be neutralized with salicylic acid. It was found necessary to filter it quickly into the ether solution of acid.

It was not determined whether the cloudiness was due to a polymerized decomposition product or to the free base itself, which in this case would be an internal salt and not very soluble in ether.

### XI. *m*-Hydroxyphenyl-isourea Salts

(1) Cyanamide and resorcinol in equimolecular proportions were dissolved in ethylene chlorhydrin. The reaction was slow and the isourea hydrochloride was obtained as a red oil when the reaction mixture was poured into ether.



The free base liberated in the usual way underwent a rapid change in the ether solution and a brown gummy solid separated which was difficult to filter off. Sufficient base was obtained, however, to give, with salicylic acid, a salt crystallizing in silky flakes from a mixture of methyl alcohol and ether; m.p., 138.5° C. Calcd. for  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_5$  (mono-isourea): N, 9.65%. Found: N, 9.82, 9.95%.

(3) *Benzoate*

Compact crystalline powder from alcohol; m.p., 128° C. Calcd. for  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_4$ ; N, 10.22%. Found: N, 9.96%.

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## THE ALKALOIDS OF PAPAVERACEOUS PLANTS\*

### XXIII. *GLAUCIUM FLAVUM* CRANTZ<sup>1</sup>

BY RICHARD H. F. MANSKE<sup>2</sup>

#### Abstract

An exhaustive examination of *Glaucium flavum* has revealed the presence of luteanine, isocorydine, aurotensine, and alkaloid F47 (not yet characterized), in addition to the two alkaloids already known to be present, namely, protopine and glaucine.

It is the opinion of the author that the chemical constituents of a plant are as definite indicators of identity as are taxonomic features. Furthermore, since the identity of the chemical constituents is not a matter of personal interpretation, as are the characters of many criteria used by systematic botanists, it seems reasonable to assume that the nature of the chemical constituents may yield important clues not only in pointing to affinities within genera and families, but in defining species limits. The labour involved in isolating and characterizing the alkaloids of all the plants of the Papaveraceae family is admittedly enormous, but, since the purely chemical knowledge thus obtained would in any case justify the effort, the incidental contribution to botanical knowledge can be regarded as a welcome by-product.

The genus *Glaucium* is represented by some 20 species but in many cases the species limits are ill-defined. A variety of one authority may be given specific rank by another or it may be reduced to the vague designation of a form. It seemed therefore of interest to investigate in considerable detail a well known and recognizable species, the identity of which appears to be in no doubt. Such a species is *Glaucium flavum* Crantz (*Gl. luteum* Scop.) from which Probst in 1839 (8) isolated a mixture of alkaloids which was shown by Fischer in 1901 (2) to consist principally of protopine and an alkaloid termed glaucine. Others, notably Gadamer (3), confirmed Fischer's findings, but in spite of the fact that many investigators isolated glaucine from the same source no additional alkaloids have been reported.<sup>†</sup> If it were a fact that only two alkaloids are elaborated by *Gl. flavum* it might be expected that many other species of *Glaucium* would elaborate only the same pair. Under such circumstances an attempt to elucidate moot points in botanical classification

\*Since the scope of the work on the alkaloids of fumariaceae plants has extended to the entire Papaveraceae family it is deemed expedient to number the papers sequentially from the former and include in the present title the subfamilies Hypecoideae and Papaveroideae. New alkaloids will be numbered serially following those in previous papers.

†Fischer's claim to have isolated sanguinarine and chelerythrine has not been substantiated and is probably based upon inadequate identification.

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by chemical methods would fail. It was therefore desirable to make a serious attempt to find other alkaloids, and in fact no fewer than four additional ones have been found. The isolation procedure which the author has used repeatedly was applicable in the present case and no difficulty was encountered in the isolation of pure protopine and glaucine. The mother liquor from the latter yielded an appreciable quantity of luteanine, an alkaloid first found in *Corydalis lutea* (7). It was present to the extent of 0.018%, a figure which compares favourably with the protopine content of 0.046%. Two phenolic alkaloids were found in their appropriate fractions, namely, isocorydine (but no corydine) and aurotensine. The fourth alkaloid (F47) appears to be new but owing to the minute amount obtained it could not be adequately characterized. It is proposed to investigate other species of *Glaucium* as well as some named varieties of *Gl. flavum* and it is expected that alkaloid F47 may become available in larger quantities.

The presence of aurotensine (6) calls for comment in that protoberberine alkaloids are not elaborated by most of the genera included in the Papaveraceae. Isocorydine differs from glaucine chiefly in the relative positions occupied by the O-substituents, and the co-presence of the two types has been commented upon in a previous paper (5). Incidentally, it may be mentioned that glaucentrine (6) could not be found although it had been expected that, in view of the large amount of glaucine, it would be found in fair quantity.

### Experimental

The material for this investigation was collected on the Suffolk Coast of England by the late Prof. George Barger and his colleague Prof. John Walton of the University of Edinburgh. The author takes great pleasure in expressing his indebtedness to these scientists, a pleasure which is not unmixed with regrets at the untimely passing of Professor Barger.

There was available a total of 28.8 kilos of dried material comprising young and mature plants as well as the roots. It is therefore probable that all alkaloids elaborated by this plant at any stages of its growth were present in the material. At no point in the isolation of the bases was there obtained an alkaloid resembling chelerythrine or sanguinarine, although the final uncrystallized bases from the combined mother liquors weighed less than 0.3 gm. The isolation procedure repeatedly employed by the author has been followed and the same designations of the various fractions are used (4). It was observed that shaking the aqueous acid solution (S) with chloroform yielded a permanent gel. This was avoided by dropping the chloroform in a fine stream into the aqueous solution until most of the glaucine had been removed. Extraction could then be completed by shaking with the chloroform. The following is a summary:—

Base hydrochlorides extracted from aqueous solution by means of chloroform—

BC—Non-phenolic bases,—glaucine, luteanine, alkaloid F47.

EC—Phenolic bases extracted from alkaline solution by means of ether,—isocorydine.

Base hydrochlorides not extracted from aqueous solution by means of chloroform—

BS—Non-phenolic bases,—protopine.

BSE and EES—Phenolic bases precipitated by carbon dioxide,—aurotensine.

The other fractions not here listed were either very small or contained traces of the alkaloids already named.

*Glaucine, Luteanine, and Alkaloid F47*

The crude fraction (BC) was thoroughly washed by decantation and then by kneading in warm water. After thorough air drying it was suspended in several litres of dry ether and the successive decantates were filtered through a layer of charcoal. The combined extract was evaporated to about 700 cc. and seeded with a nucleus of glaucine. The filtrate from the crystalline glaucine was evaporated to 200 cc., whereupon another crop of glaucine crystallized. The yield of not quite pure glaucine at this point was 150 gm.

The ether was removed from the final filtrate and the resinous residue dissolved in 400 cc. of water containing enough oxalic acid to render the solution acidic to Congo red. The filtered solution was repeatedly extracted with ether. (The semisolid extract which remained from the evaporation of the ether was extracted twice with hot dilute hydrochloric acid and the solution basified with ammonia. Ether then extracted a small amount of a base which remained as a resin when the extract was evaporated. This was virtually insoluble in ether and only sparingly soluble in methanol. In contact with a little chloroform-methanol it dissolved and almost immediately crystallized. It was recrystallized from chloroform-methanol and then consisted of colourless fine needles melting not quite sharply at 280° C.\* Alkaloid F47 as thus obtained dissolved in sulphuric acid to yield a yellow solution which on heating became first dark and then purple with a brown cast. The yield was somewhat less than 0.1 gm.) The aqueous solution was then basified with ammonia and the liberated bases were extracted with ether. The washed and dried (potassium hydroxide) extract was evaporated to 100 cc. and seeded again with glaucine. The crop of crystals was removed and the bases in the filtrate were recovered and dissolved in dilute hydrochloric acid. The aqueous solution was then extracted with chloroform (this was necessary to eliminate a small amount of protopine which is carried along into the chloroform extract (C), particularly when the latter is rich in alkaloids) and the chloroform extract evaporated. The residue was dissolved in water and the filtered solution again basified with ammonia and extracted with ether. The ether extract was evaporated to a thin syrup and set aside. The crop of crystals which formed in the course of several days was filtered off and washed with ether. It then melted at 177 to 178° C. After recrystallization from methanol-ether it consisted of colourless fine prisms which melted sharply at 183° C. In admixture with a specimen of luteanine from *C. lutea* there was no depression of the melting point and the colour reactions with

\*All melting points are corrected.



sulphuric acid of the alkaloid from both sources were identical and as follows: in the cold a colourless solution which on heating became bluish-olive only near the boiling point of the acid. The latter colour remained on cooling the solution. The optical activity in methanol was  $[\alpha]_D^{30} + 205^\circ$  ( $c=0.4$ ). Luteanine yields a hydrobromide which can be readily recrystallized from methanol, in which it is only moderately soluble.

The ethereal filtrate from the luteanine contained only a mixture of luteanine and glaucine. The hydroiodide of glaucine is only sparingly soluble in water (1) while that of luteanine is moderately soluble. A dilute acetic acid solution of the bases from the mother liquor was treated with sodium iodide until no more crystalline precipitate was obtained. The precipitate consisted of the hydroiodide of glaucine. The bases in the filtrate were regenerated and the luteanine was crystallized as far as possible. A repetition of the iodide precipitation on the ultimate mother liquor yielded a further small amount of glaucine and a little more luteanine, but no other bases. The total yield of glaucine was 193 gm. (0.67%) and that of luteanine was 5.2 gm. (0.018%).

#### *Protopine*

The isolation of protopine in a pure state from fraction (BS) was in this case most conveniently accomplished as follows. The dark amorphous base was dissolved in dilute hydrochloric acid and the filtered solution diluted to about one litre. It was basified with excess ammonia and shaken with several litres of ether. A large volume of the latter is necessary to avoid the crystallization of the protopine in the separatory funnel. The washed solution was rapidly evaporated and the residue heated with a little methanol. The protopine which crystallized at once was filtered off and recrystallized from chloroform-methanol. It melted either alone or in admixture with an authentic specimen at  $210^\circ\text{C}$ . The total yield of protopine was 13.5 gm. (0.046%). The final mother liquor contained a small amount of glaucine which was removed by extracting a hydrochloric acid solution of the bases with chloroform. There was ultimately obtained a colourless resinous base weighing about 0.1 gm. which could not be induced to crystallize.

#### *Isocorydine*

The fraction (EC) as first obtained was contaminated with a considerable amount of glaucine and luteanine which were removed by reprecipitation with excess potassium hydroxide. The alkaline filtrate was saturated with carbon dioxide and the base extracted with ether. The residue from the ether extract was converted to hydrochloride in methanol and crystallization hastened by adding ethyl acetate and ether. The hydrochloride was recrystallized from methanol-ethyl-acetate and the free base regenerated by means of ammonia and extracted with ether. The extract was evaporated to a thin syrup and treated with hexane until the incipient turbidity just disappeared on mixing. The large colourless crystals thus obtained melted sharply at  $184^\circ\text{C}$ ., and admixture with a specimen of isocorydine from *Dicentra canadensis* did not lower the melting point. The total yield was not more than 0.1 gm.



(4 p.p.m.). Corydine could not be detected although its sparingly soluble hydrochloride would have made detection facile.

#### *Aurotensine*

The fractions (BSE and EES) contained only a small amount of material and were combined. Treatment with hydrogen chloride in methanol readily yielded a sparingly soluble hydrochloride which was filtered off and washed with methanol. Calcd. for  $C_{19}H_{21}O_4N \cdot HCl : OMe$ , 17.08%. Found: OMe, 16.92%. The hydrochloride was suspended in water, ammonia added, and then shaken with ether. Crystallization took place before all of the ether had been evaporated and was hastened by the addition of a trace of methanol. The base was recrystallized from methanol and obtained in pale pink rectangular plates which melted with gas evolution at 126 to 127° C. In admixture with a specimen of aurotensine from *Corydalis ochotensis* it melted at the same temperature. The colour reactions in sulphuric acid of the base from the two sources were identical. The total yield, including a small amount obtained from fractions (BCE and EEC), was 1.1 gm. (38 p.p.m.).

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## TIME OF SET OF SILICA GELS

IV. THE EFFECT OF ALDEHYDES AND SUGARS OVER A pH RANGE<sup>1</sup>BY L. A. MUNRO<sup>2</sup> AND J. A. PEARCE<sup>3</sup>

## Abstract

The effects of a series of sugars, aldehydes, and other substances on the time of set of silica gels have been investigated over a pH-range. Diacetone alcohol, propionaldehyde, rhamnose hydrate, and xylose give curves similar to those previously obtained with the alcohols having a constant and equal effect at pH 7. The hexoses behave as a group while the disaccharides show divergent effects. Propionaldehyde and acetone give very similar curves. The implications of the results are discussed.

Previous investigations (2, 3, 4) have shown a striking regularity in the molar effect of alcohols on the time of set of silica gels. At pH 7.0, mono- and polyhydric alcohols in 0.5 *M* concentration gave gels having a setting time 106 to 108% of the time of set of the control gel. For alkaline gels the effect of the addition agents became markedly specific.

The present study was undertaken to determine whether a series of aldehydes and sugars showed a regularity of behaviour as addition agents, and also whether at pH 7.0 or some other hydrogen ion concentration a constant effect was obtained.

## Experimental

The technique used was the same as that previously described (2, 3, 4). Since the concentration of silica has little influence on the percentage effect on the time of set, a different concentration of silicate was selected for this study to give mixtures setting in a more convenient time-range. This silicate had a specific gravity of 1.0613 and contained 2.87% SiO<sub>2</sub>. Twenty-five cubic centimetre portions of this were used in each 50 cc. of gelating mixture.

The best grades of the following addition agents were used in the investigation: acetone, diacetone alcohol\*, aldol\*, xylose (two sources), rhamnose hydrate (three sources), dextrose (anhydrous; two sources), dextrose hydrate, levulose (three sources), galactose (four sources), mannose (three sources), maltose (two sources), sucrose (commercial), formaldehyde, acetaldehyde, propionaldehyde, *n*-butyraldehyde, isobutyraldehyde, paraformaldehyde, paraldehyde.

## Results

The results are tabulated in Table I. The first line gives the pH of the control gels ( $\pm 0.02$  pH units). Line 2 records the volume of standard acetic acid (1.636 *N*) in the acid mixture (acetic acid + water + addition

\* Kindly supplied by Prof. J. A. McRae, Queen's University.

<sup>1</sup> Manuscript received September 16, 1939.

Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario, Canada.

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TABLE I

THE EFFECT OF ADDITION AGENTS, PRESENT IN 0.5 M CONCENTRATION,  
ON GELS DIFFERING IN pH

pH	9.50	8.55	7.70	6.70	5.50
Cc. acid	13.0	14.0	14.5	15.0	16.0
$t_c$ , control gel, min.	15.1	7.12	4.67	7.00	92.2
$t_A$ for acetone	27	56	95	119	125
Diacetone alcohol	4	42	86	117	132
Xylose	142	123	113	107	106
Rhamnose hydrate	81	89	96	111	112
Dextrose (anh.)	184	132	118	111	107
Dextrose hydrate	192	138	120	112	105
Levulose	160	137	126	115	112
Galactose	218	153	126	116	111
Mannose	177		123	112	105
Maltose	108	106	103	100	98
Sucrose	167	131	105	96	91
Formaldehyde	90	101	105	106	104
Acetaldehyde	40	57	75	100	110
Propionaldehyde	27	56	93	110	117
n-Butyraldehyde*	8	56	786	343	340
Paraldehyde**	30	70	102	136	143

\*Concentration probably not exactly 0.5 M.

\*\*Concentration 0.5 M/3 to serve as comparison with acetaldehyde.

agent = 25 cc.). Line 3 shows the time of set of the control gel in minutes for the above pH values. Subsequent lines show the effect of different addition agents when present in 0.5 M concentration. This effect is expressed as time of set with addition agent as percentage of the time of set of the control gel ( $t_A = x\%$  of  $t_c$ ). These values are the mean of from two to six determinations made with samples of the reagents from different sources.

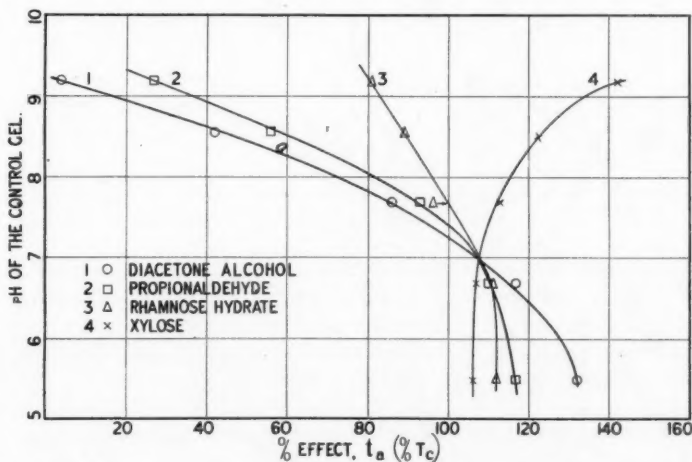


FIG. 1. The effect of various addition agents (0.5 M/l) expressed as percentage of the time for the control gel.

Except in the case of one sample of levulose, all samples gave  $t_A$  and final pH values agreeing within experimental error.

A plot (Fig. 1) of the data for diacetone alcohol, propionaldehyde, xylose, and rhamnose (hydrate) shows curves very similar to those obtained with the alcohols (4). The diacetone alcohol has a greater effect in alkaline gels than any monohydric alcohol previously studied. The curves for propionaldehyde, rhamnose hydrate, and xylose show a constant effect on the set at pH 7.0, and this effect is almost exactly the same as that previously noted, viz., 106 to 108% of  $t_c$ . Xylose simulates a pentahydroxy alcohol in its effect when the medium is alkaline, while the methylpentose behaves more like a mono- or dihydroxy alcohol.

It would be interesting to compare the effects of glucose and methylglucose and other similar compounds.

#### Hexose Sugars

The results for the hexoses and disaccharides are shown graphically in Fig. 2. It will be seen that the hexose sugars behave as a group, exhibiting little difference in their effects on the time of set. They retard the setting time over the whole pH range studied; in this respect they resemble the polyhydric alcohols. Dextrose hydrate and anhydrous dextrose give virtually the same effects. The retarding effect observed with rhamnose therefore is not due to the fact that the hydrate was used.

The curves for maltose and commercial sucrose show more individuality. Their behaviour is peculiar in that they become accelerators when the medium is acidic. Hurd and Carver (1) obtained a slight lengthening of the time of set for sucrose at pH 5.55. This would bring it more in line with the hexoses. The slight solubility of lactose in the writers' gelating mixture made im-

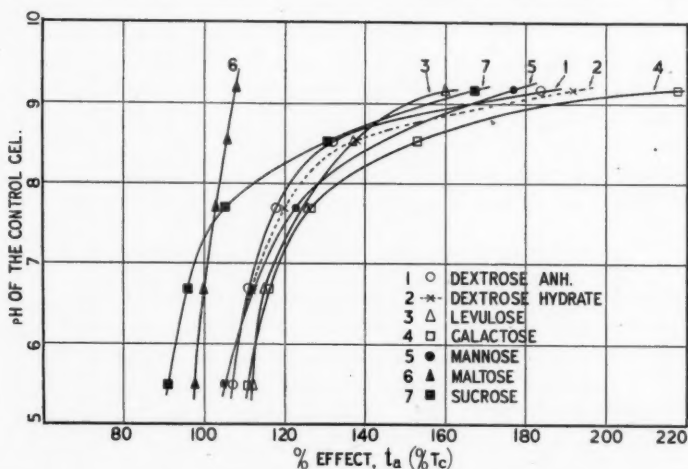


FIG. 2. The effect of sugars on the time of set.

possible a satisfactory extrapolation to 0.5 *M* for the curves. It is accordingly omitted.

### The Aldehydes

Considerable difficulty was experienced in the study of the aldehydes. It was found that the solubility and other properties changed rapidly, particularly in the cooling thermostat, owing to polymerization. The solubilities of *n*- and isobutyraldehyde, aldol, paraformaldehyde, and paraldehyde are such that results do not represent the effect of 0.5 *M* concentration. However, in so far as could be determined, *n*- and isobutyraldehyde had almost identical effects. These, with paraldehyde and aldol, are accelerators between pH 8.0 and 11.0 and retarders when the medium is acidic. They will have in all cases more pronounced effects than propionaldehyde. Paraformaldehyde was virtually insoluble in the writers' mixtures.

Curves showing the effects of formaldehyde, acetaldehyde, and *n*-propionaldehyde are given in Fig. 3. The curve for acetone is also included. It will

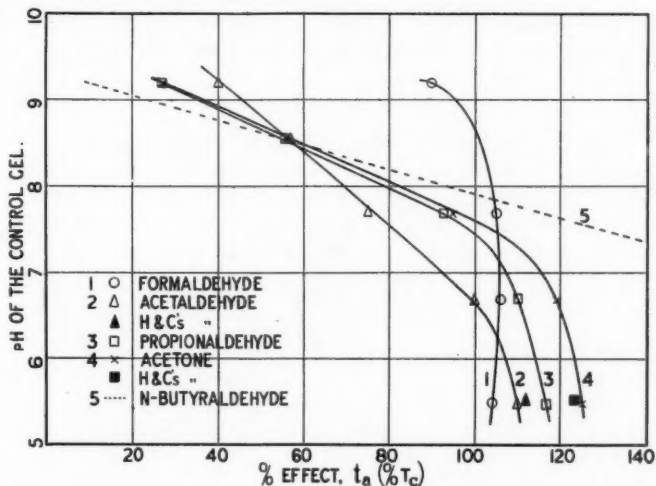


FIG. 3. The effect of aldehydes and acetone on the time of set. Hurd and Carver's values for acetaldehyde and acetone are shown by solid points.

be noted that the curve for the ketone is almost identical with that for the aldehyde containing the same number of carbons (methyl groups), except that in the acid region there is a slight divergence. Hurd and Carver's (1) values for acetaldehyde and acetone calculated as percentages of  $t_c$  are 112 and 123%, respectively, at pH 5.55. These are in good agreement with the writers' results.

### Discussion

Recently Tourky (5) has shown by ultra-fine filter dialysis that the maximum amount of aggregation of silicic acid occurs at pH 7.0. There is a more rapid

rate of decrease in the amount of silicic acid aggregated as the pH is increased from 7.0 to 11.0 than there is when the pH is decreased from 7.0. The similarity of behaviour of various non-electrolytes as addition agents at pH 7.0 would indicate a molecular effect virtually independent of molecular size or dielectric constant.

It is known that the effect of alkali on the sugars is very complex, involving rearrangement, decomposition, and oxidation. It is therefore improbable that solutions initially containing the same number of molecules of addition agent should give the same effect, but rather that the effect would be similar to that produced by a higher concentration, and the curve would cross the pH 7.0 line at different points. The similarity of the curves for the hexoses is of interest. The divergence of the curves for the aldehydes at pH 7.0 may again be due to a change in the number of molecules present. As with the sugars, the complexity of the system renders difficult any theoretical deductions. The study shows, however, the effect on the time of set obtained when similar molar concentrations of these substances are initially present.

Tourky (5) finds also that there is no aggregation of silica beyond pH 11.0. This is in agreement with the writers' observations (4).

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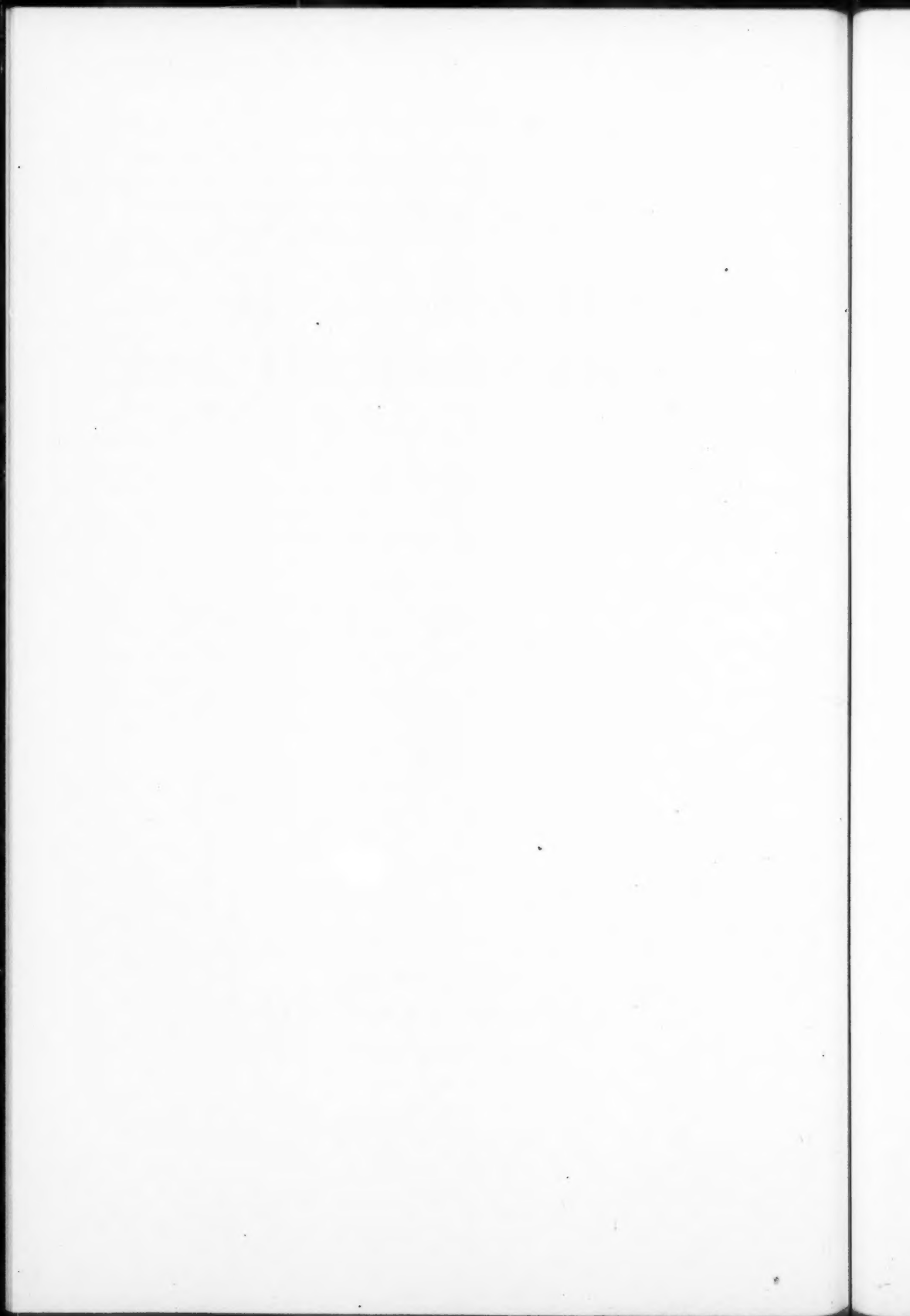
SECTION B



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### Errata

Page 53, second paragraph under "Experimental", third line, for "ophiocarpine (F40)" read "ophiocarpine (F39)", and for "alkaloid F39" read "alkaloid F40".

Page 318, third line of abstract, for "glass, wool and celanese" read "glass wool and celanese".

Page 318, third paragraph, first line, for "*k*" read "*K*".

